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Nineteenth Century Chemistry and Twentieth Century Needs

The Mill Chemist as an Economic Advantage—Chemist's First Duty—Progress in Rayon, Cotton and Wool Chemistry—Opportunities Open for Greater Work

By ALAN A. CLAFLIN

ANDREW CARNEGIE was the first American steel maker to employ a chemist. In his autobiography Carnegie does not hesitate to proclaim his acumen in availing himself of the services of a scientist at a period when his competitors scoffed at the idea of a laboratory contributing anything to the knowledge or practice of steel making. Not so long after Carnegie employed his chemist, other industries felt the urge, and so about fifty years ago the chemist made his appearance in the American textile industry.

True, only a few of the larger mills took this radical step at first. But the beginning was made and from that time to this the number of chemists employed by the textile interests has steadily increased, until now it is only the small and backward mill that does not have at least one chemist on its staff. Unfortunately, the value of the chemist to the individual employer has varied almost exactly in inverse ratio to the number of chemists employed. When Carnegie's chemist showed him he could buy his neighbor's cinder-pile at one-tenth the price of Lake Superior ore and make as good steel from it, that gave Carnegie a tremendous economic advantage. When one mill bought its Indigo on analysis and competitors bought on guess, that item alone paid the chemist's salary. When all mills have chemists to test their purchases, none have particular advantages over the others; the chemist's salary, like the cost accountant's, becomes just one of the added expenses of doing twentieth century business.

It is a mistake, however, to believe that because certain work of the chemist has become routine, it is not just as possible to-day as it was fifty years ago to gain economic advantages over competitors by scientific assistance. To accomplish this it is essential that the chemists employed be as far in advance of the daily routine as was the case half a century ago. Such men are available; they are to be found in universities; they are not, however, recent graduates of elementary technical institutions.

Research Not an Economic Hazard

Inasmuch as chemistry has been advanced, extended and ramified, no one man possesses requisite knowledge; a group of specialists is now required. Relatively it may be no more of an economic hazard for a large textile corporation to create an adequate research laboratory than it was fifty years ago for a single mill to invest in the services of one chemist and give him a small laboratory. But the problem of convincing those who have the financial responsibility of the success of such an enterprise is more difficult, because of the extensions and ramifications of present-day chemical science.

To some degree methods of technical instruction are to blame for this condition. Fifty years ago a man who had training in general chemistry was turned loose in a textile plant. He brought to it a new point of view, new methods and little rigidity of precedent. To-day a man is usually educated as a textile chemist; he is given the mill viewpoint before he has grasped the philosophy of a science; he is a somewhat trained worker, but in channels already charted for him. He may know a little more analytical chemistry than the dyers and color mixers; he may have a little more familiarity with organic structural chemistry; but he soon becomes merely a *routine* laborer or executive with narrowly prescribed duties and responsibilities, and with slightly, if any more, opportunity for study, and the exercise of his imagination and initiative than is allowed any overseer.

It is now generally recognized by scientists that textile chemical problems are of that class known as colloidal

chemistry, but how many textile chemists to-day know any colloidal chemistry? Practically none. It is further recognized that those who are contributing to the advance of knowledge of colloidal chemistry are the physical chemists, but how many mill chemists to-day are physical chemists? Again the answer is, practically none.

In the desire to develop men who may be immediately useful we sacrifice the possibility of training men to be of ultimately much greater value. The analysis of the chemical agents used in the manufacturing processes, the accurate testing of dyes, are duties essential to the successful operation of a mill; but they are not duties which should occupy much of a chemist's time or attention. If he cannot train a lad (or, perhaps better, a young woman) in a short time to do the routine testing, he is hardly qualified for the position of chemist. The selection of processes and products, the choice of dyes for given purposes, are far more important, both for the intellectual capacity involved and in the ultimate value to the mill, than problems of ordinary testing; but frequently in these important matters the chemist is only one of several consultants, and sometimes little if any weight is given his opinion.

Chemist's First Duty

One circumstance always brings the chemist into his own and that is trouble. It is true that since clinics have become common he is not so often called to administer first aid in accident cases, but when a boiler scales, or piece goods are shaded, colors fade or warps chafe, the chemist's aid is sought, and usually before his surmise or guess is verified or refuted, the trouble is corrected by those more intimately associated with the process. Unquestionably it is the first duty of the chemist to make sure, so far as chemical questions are involved, that all processes of the mill are conducted as nearly as possible to the point of maximum efficiency; that control methods are so devised that chemical variables are eliminated, if *human* variables cannot be; that products are duly tested and properties of dyestuffs tabulated and catalogued. Only in this way can the failure of colored fibers to withstand the rigors of processing or of fabrics to meet all requirements of the selling houses be certainly known in *advance;* only in this way can one avoid the unexpected and undesired.

Such results as these, while they may not be perfectly attained in daily practice, should not be the end-all of the ambition of the twentieth century chemist. They may have represented the goal of the chemist a generation ago, but chemical science has progressed since then. The chemist to-day should be sufficiently familiar with modern knowledge and modern methods to begin to apply them to those processes—and they are many—which are still governed by the experience of the individual or by traditions handed down by generations of rule-of-thumb workers.

As yet there has been little progress in this direction. The textile industry so far as chemistry is concerned has not advanced beyond the end of the last century, with one glorious exception. This exception, the synthesis of commercial fibers, has not been due to the textile chemists themselves, but to the initiative of workers in other fields. Indeed, textile chemists more often complain of the shortcomings of rayon as compared to the natural fibers rather than feel in its development a tremendous inspiration to study the chemical constitution and structure of the *natural* fibers.

Since the most successful commercial synthetic fibers have a cellulose base, coincident with their production has come a knowledge of the cellulose molecule. The stereochemistry of this molecule established, the orientation of these molecules in the natural vegetable fibers has been ascertainable by investigators employing the distinctly modern method of X-ray photography.

As yet in textile circles there has been little attention paid to this epoch-making demonstration. Undoubtedly the value of the work is more generally recognized in Germany than in America, and if it had been accomplished in Perlin rather than California, it would have received more publicity. Because our standards of chemical knowledge in the textile industry are low, its significance is generally unappreciated. For the textile chemist working with cotton, the field of his work has become brilliantly illuminated by the purely scientific investigators of the university laboratories. One may not, however, find his way in the daylight more easily than in the dark if he does not know whither he is bound; knowledge of the crystalline structure of the cotton fiber will be of little value if the removal of associated impurities depends merely on the efficiency of empirical processes.

Importance of Wool Studies

With wool there has yet been little modern scientific work done. While the various amino bodies resulting from the decomposition of wool have been tabulated and fairly well studied, that work was completed forty years ago. Although much data have been gathered on the iso-electric point of hide substance, and its reactivity with tanning agents on both sides of this point, those who have to do with wool have not known sufficient modern chemistry to have competent men determine the same information about wool. Wool is really a more attractive subject for investigation than cotton because of its far greater chemical activity, or in modern language, the greater ionization of certain of its radicals in the presence of ions of opposite electrical charges in aqueous solution. Practically all dyeing operations on wool are done in acid solution; that is, on the acid side of the iso-electric point. Wool is reasonably active under these circumstances, as shown by its combinations with acids, mordants and dyes, and at the same time is extremely insoluble in the dispersion media, the acidified water. Of itself this behavior of wool should be enlightening as to its chemical constitution and undoubtedly ultimately will be. The alkaline

side of the iso-electric point of wool is of equal if not more importance than the acid side. All of the cleansing operations on wool are presumably conducted on the alkaline side of the iso-electric point. As the exact range of that point or zone has not been determined, it may be practically possible, as it is surely hypothetically possible, that cleansing operations should be conducted very close to the iso-electric point. Consideration of the wool fiber from this view emphasizes the importance of potentiometric determinations, while in acidified dispersion media the fiber is very insoluble. On the alkaline side as the concentrations of hydroxyl ions is slightly (in a relative sense) increased, the ionization of constituent radicals becomes so great that the fiber disintegrates and ceases to be wool at all, becoming instead of an organized colloid in a dispersion media, a solution of alkaline salts of amino acids.

The immense practical importance of considering the behavior of wool in relation to hydrogen ion concentration may be understood by drawing an analogy between the old-fashioned housewife who baked her bread by guessing when the oven was hot enough and the thermostatic control in modern bakeries, or even in the newer household ranges. Because the experience is considerable, and the operations conducted very slowly, as much wool is not damaged in the scouring process as might naturally be expected. Neither did the old-fashioned housewife spoil as much bread as might have been expected, It is, however, not creditable to an industry to have important operations conducted by guesswork even if those who do the guessing, guess extremely well

Natural Fibers Maintain Their Place

In all probability natural fibers will be for a long time pre-eminent in the textile industry, not only because of the persistence of habit and custom, but also because investigation and cumulative research gain slowly toward the perfection attained by nature and because under modern conditions there is ever the greater inducement for early exploitation rather than ultimate perfection. This, however, should not be taken by the textile chemist as a foregone conclusion. Rayon fibers lack the tensile strength of cotton because the arrangement of the cellulose molecules in relation to each other or, as the physicists say, their orientation, is not so symmetrical.

Recent developments in rubber chemistry indicate the control of the orientation of the rubber molecule by an electric current in such a manner that films are formed of almost unbelievable strength. It requires no great stretch of the imagination to expect similar methods to be utilized in the production of rayons or other synthetic fibers of a strength far surpassing the natural fibers. It is not to be expected, however, that the texile chemist unaided can apply all the modern learning to the art with which it is connected. There are great agencies of research all around him; greater ones are to be established. It is the duty of the textile chemist to be sufficiently familiar with the trend of chemical thought to recognize discoveries that really shed new light on his problems, and disclose new methods for him to use in conquering those problems. The employer of the chemist should be sufficiently enlightened to appreciate that his chemist is not, as he was formerly sometimes regarded, a guardian of secrets, but a scout to ascertain what is being done in the industry—an adviser working to make sure his mill is abreast of the times, and where possible invoking the assistance of the specialists of the universities that his mill may be in the van of progress. Instead of complaining that the papers presented at the chemical meetings he attends are so advanced that he does not understand them, his employer should feel grateful that he is engaged in a progressive science. Let the textile chemist be stimulated by the thought that there is so much for him to learn and that the present backward state of his industry chemically means all the greater opportunity for him to prove his value to it.

FAST UNIFORM COLOR SOUGHT

The United States Government is seeking a fast color for cotton uniforms. A standard olive-drab cloth was chosen in 1909 and is now in use. Atlhough it was adopted only after exhaustive tests, it has never been absolutely fast. Effects of repeated laundering have been noticeable, and it has finally been decided to make further research in hopes that a faster shade will be discovered. The Color Laboratory of the Bureau of Standards has, of course, been called upon to assist in the search, and this bureau in turn has enlisted the services off several dyestuff firms, textile mills and other authorities.

The fall initiation of Eta Chapter of Phi Psi, professional textile fraternity at State College, was featured by the election of F. Gordon Cobb, general superintendent of the Lancaster Cotton Mills, Lancaster, S. C., as an honorary member of the fraternity. Mr. Cobb is one of the leaders of the textile industry in the South, and is now secretary of the Southern Textile Association. At the last meeting of this body he was awarded a gold medal for the most notable work in the textile industry of the South during the past year.

Walter C. Taylor, Charlotte, N. C., sales representative of the Duplan Silk Corporation, and a graduate of the State College Textile School, Raleigh, made an interesting and instructive talk to the textile students of State College on December 9. Mr. Taylor, who was formerly production manager for a chain of silk mills in Paterson, N. J., spoke on the cultivation and manufacture of silk. He prefaced his remarks by telling the students that the textile industry offered a wonderful future to technically trained men who acquire practical experience in the industry.

Foreign Dyes Imported Through New York and Other Ports During November

Compiled by the Chemical Division of the Bureau of Foreign and Domestic Commerce in Collaboration with the Chemical Division of the United States Tariff Commission

KEY TO ABBREVIATIONS OF MANUFACTURERS' NAMES

1—THE SIX LEADING GERMAN COMPANIES

IG—Interessen-Gemeinschaft der Farbenindustrie.
A—Actien-Gesellschaft fur Anilin-Fabrikation, Berlin. Founded 1873.
B—Badische Anilin-und-Soda-Fabrik, Ludwigshafen-on-the-Rhine. Founded 1865.
By—Farbenfabriken, vormals Friedr. Bayer & Co., Leverkusen-on-the-Rhine. Founded 1862.
C—Leopold Cassella & Co., Frankfort-on-the-Main. Founded 1870.
K—Kalle & Co., A. G., Biebrich-on-the-Rhine. Founded 1870.
M—Farbwerke, vormals Meister Lucius & Bruning, Hochst-on-the Main. Founded 1862.

2—THE SMALLER GERMAN COMPANIES

BK—Leipziger Anilinfabrik Boyer & Kegel, Furstenberg. near Leipzig. Founded 1882.
CG—Chemikaliewerk Griesheim G. m. b. H., Griesheim-on-the-Main. Founded 1882.
CJ—Carl Jager G. m. b. H., Anilinfarbenfabrik, Dusseldorf. Founded 1823
GrE—Chemische Fabrik Griesheim-Electron, Offenbach-on-the-Main. Founded 1842.
L—Farbwerk Mulheim, vormals A. Leonhardt & Co., Mulheim-on-the-Main. Founded 1879
Seig.—G. Seigle Corporation, Stuttgart.
tM—Chemische Fabriken, vormals Weiler ter Meer, Uerdingen-on-the-Rhine. Founded 1877.
WD—Wulfing, Dahl & Co., A. G. Barmen. Founded 1842.

3—SWISS COMPANIES (ALL AT BASEL)

DH—Farbwerke vormals L. Durand, Huguenin & Co. Founded 1871.
G—Anilinfarben-und Extract-Fabriken, vormals Joh. Rud. Geigy. Founded 1764.
I—Gesellschaft fur chemische Industrie. Founded 1885.
S—Chemische Fabrik, vormals Sandoz & Co. Founded 1887

4—DUTCH AND FRENCH COMPANIES

FA—Farbwerk Ammersfoort, Ammersfoort, Netherlands. Founded 1888
NF—Niederlandische Farben-und-Chemikalienfabrik Delft, Delft, Netherlands. Founded 1897.
CN—Compagnie Nationale de Matieres Colorantes et Produits Chimiques. Founded 1917. (Etablissements Kuhlmann merged with this company in 1923.)
P—Societe Anonyme des Matieres Colorantes et Produits Chimiques St. Denis (formerly A. Poirrier). Founded 1830.

5—ENGLISH COMPANIES

Bro—Brotherton & Co., Ltd., City Chambers, Leeds.
BAC—British Alizarine Co., Ltd., Manchester
BD—British Dyestuffs Corporation, Ltd., London.
Cl Co.—The Clayton Aniline Co., Ltd., Clayton, Manchester.
CV—The Colne Vale Dye & Chemical Co., Ltd., Milnsbridge, Huddersfield.
Hol—L. B. Holliday & Co., Ltd., Huddersfield.
Scot—Scottish Dyes, Ltd., Grangemouth.

FOREIGN dyes imported through New York and other ports during the month of November totaled 383,142 pounds, valued at $327,164, a decrease of more than 77,000 pounds from the October figures. Imports by ports were as follows: New York, 371,165 pounds, with an invoice value of $313,964; Boston, 11,867 pounds, with an invoice value of $13,008; Los Angeles, 110 pounds, valued at $192.

Imports of Synthetic Dyes

	1926		1925	
	Pounds	Invoice Value	Pounds	Invoice Value
January	190,459	$184,018	403,984	$359,376
February	479,027	477,255	373,259	365,268
March	487,804	435,891	527,964	488,501
April	437,526	401,606	451,005	426,141
May	392,739	343,745	370,271	347,904
June	333,319	317,896	376,668	333,654
July	351,425	303,079	420,849	400,366
August	380,414	298,159	330,674	303,612
September	387,533	322,446	298,858	285,642
October	460,351	406,167	537,312	471,466
November	383,142	327,164	414,755	295,885
Total	4,283,739	$3,817,426	4,505,599	$4,077,815

Dyes and Intermediates Remaining in Bonded Customs Warehouse

	Coal-Tar Dyes and Colors (pounds)	Coal-Tar Intermediates (pounds)
June 30, 1926	671,396	772,475
July 31, 1926	512,186	781,796
August 31, 1926	557,852	690,031
September 30, 1926	395,535	590,520

Pert Cent of Dyes by Country of Shipment

	1926			
	Nov.	Oct.	Sept.	Aug.
Germany	50.0	48.0	50.0	47.0
Switzerland	28.0	30.0	30.0	34.0
France	4.0	6.0	3.0	2.5
England	4.0	5.0	5.0	0.5
Belgium	7.0	4.0	3.0	5.5
Canada	5.0	5.0	7.0	8.5
Italy	2.0	2.0	2.0	2.0
Holland	—	—	—	—

Five Leading Dyes, by Quantity, Imported During November, 1926

	Pounds
Rhodamine B (single strength)	17,750
Ciba Red 3B (single strength)	15,339
Indanthrene Olive R (single strength)	13,792
Ciba Violet R Paste	13,228
Alizarine Paste	11,424

The dyes in this report are grouped by both Colour Index and Schultz numbers, and, in the case of those which could not be identified by either number, the classification according to the ordinary method of application was adopted. As the pastes and powders of the vat dyes vary widely in strength and quantity, each vat dye has been reduced—in nearly every case—to a single-strength basis.

DYES OF COAL-TAR ORIGIN

Index No.	Schultz No.	Name of Dye and Mfr.	Quantity (pounds)
16	137	Fast Yellow Extra—(IG)	
		Fast Yellow S—(IG)	250
21	34	Chrysoidine RL Base—(IG)	25
32	182	Brilliant Sulphon Red 10B—(S)	1,000
40	58	Chrome Orange R—(DH)	220
54	64	Sorrel Red X—(IG)	1,000
70	—	Rapid Fast Red GL Paste—(IG)	2,000
80	83	Ponceau—(Sieg)	25
104	—	Metachrome Olive Brown G—(Bro)	2,000
105	88	Acid Anthracene Brown R—(IG)	200
124	129	Chromazone Red New Conc.—(G)	220
130	121	Erika B Extra Powder—(Q)	55
131	122	Erika GN—(IG)	100
172	159	Acid Alizarine Black R—(IG)	500
184	168	Amaranth—(Sieg)	25
278	—	Benzo Fast Rubine BL—(By)	200
288	256	Sulphon Cyanine G—(IG)	1,000
316	273	Diaminogene Blue NA—(C)	
		Diazamine Blue BR—(S)	1,265
319	—	Direct Fast Heliotrope 2RL—(By)	220
325	—	Diamine Brilliant Violet B—(IG)	100
346	296	Cotton Yellow G Extra—(IG)	100
349	—	Benzo Fast Yellow 4GL Extra—(By)	11
368	306	Ignamine Orange 3G—(B)	750
376	313	Congo Rubine B—(IG)	100
382	319	Chloramine Red B—(S)	
		Chloramine Red 3B—(S)	
		Diamine Scarlet 3B—(C)	
		Universal Bordeaux C—(IG)	2,588
394	327	Universal Violet C—(IG)	25
409	339	Diamine Orange B—(IG)	
		Diamine Orange B—(C)	1,011
423	349	Diamine Brown B—(IG)	300
430	—	Polar Red RS Conc.—(G)	551
436	358	Chloramine Brilliant Red 8B—(S)	
		Chlorantine Red 8BN—(I)	
		Toluylene Red—(IG)	3,110
443	—	Acid Anthracene Red G—(IG)	100
446	362	Diazol Fast Purpurine N8B—(CN)	551
448	363	Universal Scarlet C—(IG)	25
449	364	Diazo Brilliant Black B—(IG)	500
451	366	Deltapurpurine 5B—(Q)	550
508	415	Universal Light Blue C—(IG)	25
543	—	Diamine Brilliant Bordeaux—(R)	100
561	449	Chlorazol Brown LF—(BD)	
		Trisulphon Brown B—(S)	2,100
578	459	Universal Dark Blue C—(IG)	25
590	471	Polyphenyl Blue GC—(G)	1,102
593	474	Universal Dark Green C—(IG)	25
598	477	Diphenyl Brown GS—(G)	551
639	22	Xylene Light Yellow 2G—(S)	1,000
640	23	Tartrazine—(Sieg)	50
645	—	Kiton Fast Yellow 3G—(I)	110
653	—	Pyrazol Orange G Conc.—(S)	1,000
658	496	Rhoduline Blue 6G—(IG)	
		Setoglaucine Conc.—(G)	820
667	503	Benzyl Green B—(I)	
		Acid Green SGX Powder—(B)	562
670	505	Light Green SF Yellowish—(Sieg)	
		Light Green SF Yellowish—(IG)	155
671	506	Erioglaucine AP—(G)	4,409
672	507	Xylene Blue VS Conc.—(S)	1,000
680	515	Methyl Violet—(Q)	
		Methyl Violet Base—(IG)	
		Methyl Violet NFB—(IG)	4,031
681	516	Crystal Violet—(Q)	
		Crystal Violet Extra—(IG)	910
682	518	Ethyl Violet—(IG)	1,000
696	528	Fast Acid Violet 10B—(By)	11
704	536	Alkali Blue 3RC Conc.—(IG)	
		Alkali Blue 4R—(IG)	750
707	539	Opal Blue Bluish—(IG)	
		Water Blue—(IG)	150
710	541	Brilliant Sky Blue G—(By)	100
712	543	Patent Blue V—(IG)	2,000
714	545	Brilliant Acid Blue A—(IG)	
		Kiton Blue A—(I)	
		Poseidon Blue BXX—(IG)	1,121
715	546	Blue FF—(IG)	
		Cyanol Extra—(C)	
		Cyanol FF—(C)	
		Xylene Cyanol FF Extra—(S)	2,018
721	552	Chromal Blue GC—(G)	331
723	554	Chrome Azurol S Conc.—(G)	551
727	557	Chromal Violet—(G)	110
729	559	Victoria Pure Blue BO—(IG)	1,000
731	560	Night Blue—(B)	300
735	564	Naphthaline Green V—(M)	329
743	570	Rhodamine S—(I)	110
749	573	Rhodamine B Extra (s. s.)—(IG)	
		Rhodamine B Extra (s. s.)—(I)	
		Rhodamine B Extra (s. s.)—(Q)	17,750
751	574	Rhodamine 3B Extra (s. s.)—(IG)	250
752	571	Rosazeine 6G Extra (s. s.)—(IG)	1,250
758	582	Fast Acid Violet R—(IG)	200
762	—	Chromorhodine BN—(DH)	441
773	592	Erythrosine—(Sieg)	
		Erythrosine Extra—(M)	55
789	—	Patent Phosphine GG—(I)	2,205
797	608	Patent Phosphine GRNTN—(IG)	
		Patent Phosphine RRDX—(IG)	1,750
814	617	Universal Yellow C—(IG)	25
815	618	Rhoduline Yellow 6G—(IG)	
		Tannoflavine T—(S)	700
827	671	Induline Scarlet—(IG)	100
828	672	Azo Carmine GX—(IG)	500
842	680	Methylene Violet 3RA Extra—(IG)	250
851	690	Diphene Blue B—(IG)	200
875	923	Fur Blue Black A—(IG)	
		Fur Brown P, NZ, NZD—(IG)	
		Fur Brown 4R—(IG)	
		Fur Gray B—(IG)	
		Fuscamine G—(IG)	1,425

Colour Index No.	Schultz No.	Name of Dye and Mfr.	Quantity (pounds)
879	—	Chromazurine G—(DH)	441
882	625	Modern Heliotrope DH—(DH)	551
892	635	Blue 1900 TCD—(DH)	220
924	660	Methylene Green G Extra Conc.—(S) Methylene Green W—(G)	3,205
971	748	Hydron Blue G Powder (s. s.)—(IG)	1,667
1027	778	Alizarine Red Paste—(G) Alizarine Red VI Extra Paste—(IG)	11,424
1033	779	Alizarine Orange A Paste—(IG) Alizarine Orange AO Paste—(BD)	1,486
1034	780	Alizarine Red S Powder—(By) Alizarine Red IWS Powder—(M)	1,451
1040	784	Alizarine Red SX Paste—(IG)	838
1053	—	Alizarine Blue WS—(By) Alizarine Sapphire Blue S7—(I) Alizarine Sapphirol WSA Powder—(By)	1,899
1064	—	Alizarine Cyclamine R—(IG)	3,881
1071	808	Alizarine Green S Paste—(IG)	882
1073	852	Alizarine Blue JR Powder—(By)	220
1075	856	Alizarine Astrol B Powder—(IG) Alizarine Blue AS Powder—(By)	954
1077	860	Alizarine Direct Blue BGAOO—(IG)	750
1085	862	Alizarine Blue Black B Powder—(IG)	300
1088	855	Alizarine Sky Blue B Powder—(IG)	3,533
1091	—	Alizarine Rubinol 5G—(IG) Alizarine Rubine R—(By) Anthra Rubine B—(K)	1,050
1095	759	Anthra Yellow GC Powder (s. s.)—(B) Vat Yellow GC Powder (s. s.)—(B)	3,104
1096	760	Vat Golden Orange G Double Paste (s. s.) —(B)	2,200
1097	761	Vat Orange RRT Paste—(IG)	4,778
1099	763	Vat Dark Blue BOA Powder (s. s.)—(IG)	400
1102	765	Vat Black BB Powder (s. s.)—(IG)	1,429
1104	767	Cibanone Violet R Powder (s. s.)—(I) Vat Brilliant Violet RR Paste Fine—(IG) Vat Brilliant Violet RR Double Paste (s. s.)—(B)	2,056
1113	842	Indanthrene Blue GCD Double Paste (s. s.) —(B)	2,156
1114	—	Vat Blue BCD Paste Fine—(B) Vat Blue BCS Powder (s. s.)—(B)	3,319
1115	843	Cibanone Blue G Powder—(I)	441
1118	849	Vat Yellow G Double Paste (s. s.)—(IG) Vat Yellow G Powder (s. s.)—(B)	5,760
1135	820	Vat Brilliant Violet RR Paste—(IG)	794
1137	824	Vat Orange 6RTK Powder (s. s.)—(IG)	800
1149	873	Vat Brown GR Paste—(IG)	2,500
1150	833	Grenalone Olive B Powder (s. s.)—(GrE) Vat Olive B Powder (s. s.)—(GrE) Vat Olive R Paste—(IG) Vat Olive R Powder (s. s.)—(IG)	13,792
1151	—	Vat Brown R Paste—(IG) Vat Brown R Powder (s. s.)—(By)	8,117
1152	—	Vat Brown G Paste—(IG) Vat Brown G Powder (s. s.)—(IG) Vat Brown G Powder (s. s.)—(By)	6,544
1155	825	Algol Red B Paste—(IG)	397
1162	831	Vat Red RK Paste Fine—(IG) Vat Red RK Powder (s. s.)—(IG)	1,200
1163	832	Vat Violet BN Powder (s. s.)—(B)	840
1165	869	Vat Brown B Paste—(By)	425
1173	793	Cibanone Blue 3G Paste—(I)	2,204
1174	—	Cibanone Green G Paste—(I)	441
1186	883	Indigo MLB/6B Powder (s. s.)—(IG)	2,500
1188	884	Brilliant Indigo BB Powder (s. s.)—(IG)	500
1190	885	Brilliant Indigo B Paste—(IG)	2,543
1211	910	Thioindigo Rose BN Powder (s. s.)—(K)	880
1212	918	Ciba Red 3B Paste—(I) Vat Red 3B Paste—(Q) Vat Red Violet RH Paste—(IG) Vat Red Violet RH Powder (s. s.)—(IG)	15,339
1217	913	Hydron Orange RF Paste—(IG)	1,000
1222	901	Ciba Violet R Paste—(I)	13,228
1227	904	Helindone Brown G Powder (s. s.)—(IG)	700
1228	907	Anthra Scarlet 2G Paste—(IG) Ciba Scarlet 2G Paste—(I) Thioindigo Scarlet 2G Paste—(IG)	9,409

UNIDENTIFIED DYES

Acid Dyes

Name of Dye and Manufacturer	Quantity (pounds)
Acid Brown RN—(G)	110
Acid Pure Blue R Supra—(G)	1,102
Acid Rhodamine BG—(IG)	1,000
Acid Violet CBB—(IG)	100
Alizarine Supra Blue A Powder—(IG)	4,000
Alizarine Supra Blue SES Powder—(IG)	100
Alkali Fast Green 10G—(IG)	783
Brilliant Acid Blue FF—(By)	551
Brilliant Milling Blue B—(IG)	1,000
Brilliant Silk Blue B—(I)	220
Brilliant Wool Blue FFR Extra—(IG)	1,250
Cloth Fast Brown 5R—(I)	220
Cloth Fast Orange G—(I)	440
Cloth Fast Red 3B—(I)	661
Erio Fast Yellow AE—(G)	55
Fast Acid Green BB Extra—(IG)	800
Guinea Fast Green B—(IG)	500
Indocyanine B—(A)	2,665
Ink Fast Black A Extra—(IG)	25
Kiton Fast Red BL—(I)	220
Milling Orange G—(IG)	200
Milling Red 6BA—(IG)	200
Milling Red NJ—(CN)	661
Neolan Blue BR—(I)	441
Neolan Blue GR—(I)	441
Neolan Green LBN Conc.—(I)	110
Neolan Pink G—(I)	110
Neotolyl Black TL Extra—(IG)	200
Onis B—(IG)	200
Onis 3B—(IG)	100
Pilatus Fast Pink B—(IG)	300
Polar Red B Conc.—(G)	551
Silk Yellow R—(IG)	600
Sulphon Orange G—(IG)	500
Supramine Bordeaux B—(IG)	100
Tropaeolin RNP—(IG)	100
Wool Blue 5B—(IG)	100
Wool Fast Orange G—(By)	441
Wool Violet RC—(G)	220
Xylene Brilliant Blue FFRX Conc.—(S)	100
Xylene Fast Blue FF Conc.—(S)	1,000

Vat Dyes

Aliarine Indigo 5R Paste—(IG)	800
Anthra Pink B Extra Powder—(B)	600
Ciba Scarlet GL—(I)	88
Grelanone Red 3BR Powder (s. s.)—(GrE)	1,496
Helindone Khaki IGG Paste—(M) Helindone Khaki IGG Powder (s. s.)—(M)	900

(*Continued on page 56*)

Proceedings of the American Association of Textile Chemists and Colorists

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SIXTH ANNUAL MEETING

Charlotte, N. C., December 3 and 4, 1926

[Editor's Note.—*The report that follows completes the Proceedings of the Sixth Annual Meeting, covering the Saturday afternoon technical session. The Saturday morning session report appeared in the December 27 issue of the Proceedings, which also included the Open Forum session.*]

SATURDAY AFTERNOON SESSION

December 4, 1926

The Saturday afternoon technical session of the Sixth Annual Meeting convened at 2.45 o'clock, December 4, 1926, in the Manufacturers' Club, Charlotte, N. C., Dr. E. H. Killheffer presiding as chairman.

Dr. Killheffer—The first paper this afternoon will be one on "Physical Tests to Determine the Effects of Chemical or Other Treatments on Yarns," by Mr. Chas. F. Goldthwait. (Applause.)

Chas. F. Goldthwait—I feel some hesitation in presenting this kind of subject to a group of chemists and dyers. The applications of it may not be obvious at once, but I think before I get through you will agree with me that the subject has some interest, it is rather practical, and that perhaps we ought to know a little more about it.

. . . Mr. Goldthwait then presented his prepared paper:

Physical Tests to Determine the Effects of Chemical or Other Treatments on Yarns

By Charles F. Goldthwait
Industrial Fellow, Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa.

As can be clearly seen from a reading of the more fundamental recent papers on textile research subjects, the solution of many of the problems of the industry lies in the application of pure physics, or of physics somewhat flavored with chemistry. Coming to some of the simpler problems such as are met with every day, there are also applications of physical methods.

In processing yarns or fabrics there arise several questions as to the effects on the goods. Aside from color and the subtleties of finish, one wants to know whether the material has shrunk in length or area, whether it has become tendered or has gained or lost some desirable elastic quality.

The Length of a Yarn Sample

Thus we encounter the old puzzle: How long is a piece of yarn? Since a more or less crinkly piece of yarn cannot be measured "as is," the first thought is to straighten it out; but when is it merely straight and when is it stretched? If a skein of two-ply cotton yarn is put into

a tensile testing machine and a very small load is applied, the yarn will stretch; if another increment of load is added, it will stretch further; then as successive loads are added and the elongations are recorded, data are accumulated for a so-called stress-strain curve. Fig. 1, curve A, is such a curve for a 54-inch skein of six complete turns of ordinary 40/2 combed peeler cotton yarn

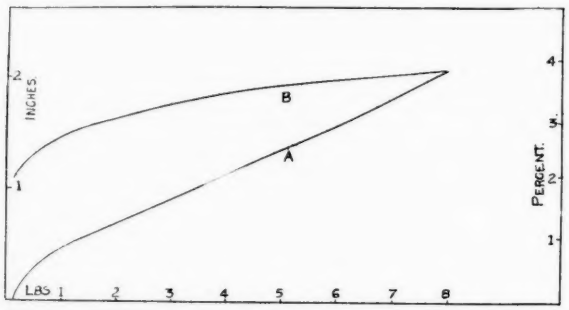
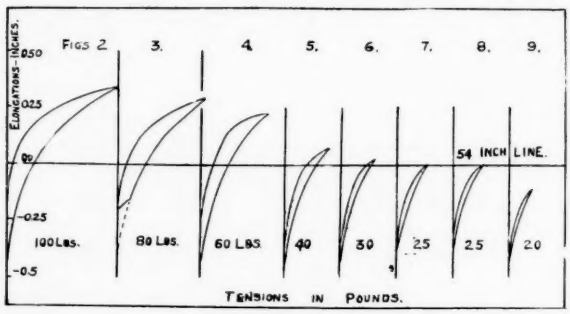


FIG. 1

at 36 per cent relative humidity. In this case the loading was stopped just short of the breaking point on certain skeins, and the yarn unloaded a little at a time, the return in length being shown by the proper curve.

Cotton yarn such as that in the present experiment is a very complicated structure consisting of possibly 150 separate fibers at each point in its cross-section, held together by nothing but twist and friction, and the twist itself is nothing but a friction device. When tension is applied, there is, as the curve shows, a complex series of events. There are a straightening of any kinks or crimps, a change in the twist angle as the component singles tend to straighten, a general tightening-up of the yarn structure, a slip of one fiber on another which extends throughout the entire yarn, and finally, perhaps, an actual stretching of the fiber substance. The break, however, except possibly in the case of very tightly twisted yarns, consists almost entirely of fiber slip and much less of actual breaking of fibers.

To go back a little, the problem was to measure yarn so that slight changes in length due to processing could



FIGS. 2 TO 9

be detected or measured. It can be seen from the stress-strain curve that the yarn did not return, under the conditions of this experiment, to its original length. The similarity in the shapes of the two curves suggests that there is something approaching elasticity in the lower part of the first. Therefore the problem was narrowed down to finding a tension at which the yarn would be straightened, at least to an arbitrary repeatable extent, without being permanently stretched.

The next series of experiments was carried out on regulation 2½-ounce skeins of cotton yarn. One represented by Fig. 2 was loaded to 100 pounds and then unloaded. Obviously it was stretched. Other skeins were put through the cycle, each to a lower maximum load than the preceding, until at 25 pounds it was found that the curve, while not exactly tracking back on itself, did come back to the same starting point. Fig. 7 shows the average of six separate skeins, while Fig. 8 shows the average path when a single skein was sent through the cycle five times. It is evident then that, for this particu-

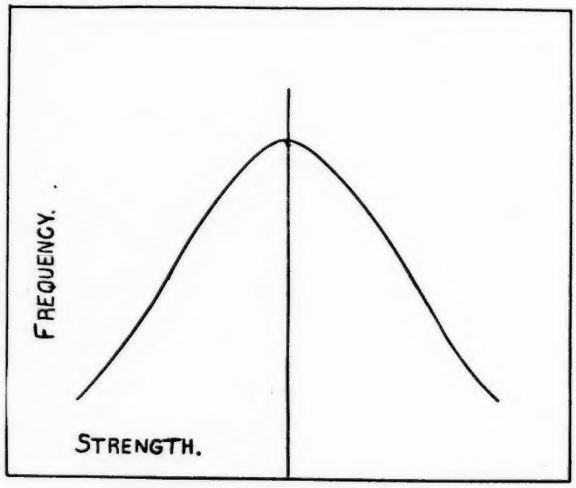


FIG. 10

lar yarn, 25 pounds, or 10 pounds to an ounce of yarn in a 54-inch skein, straightens the yarn to an extent suitable for measuring, and without making any permanent change of it.

This particular value was worked out for a particular purpose, and has proved to be very satisfactory in use. It may suggest methods of working out similar problems. An English source gives as the standard tension the weight of a lea of the yarn in question. For the above yarn this would be 50 grains, and the writer was recently agreeably surprised to find that his own method works out 50.7 grains for each "end" of yarn in the skein.

A matter of even greater importance is a test for strength, and conclusions as to the effect of chemical materials on yarns seem to be drawn at times from quite

an insufficient number of tests. While the skein or lea test is very widely used and will classify a given group of yarns in about the same order as single-thread tests, it does not meet general favor for critical work. Although made with 160 "ends" between the hooks of the

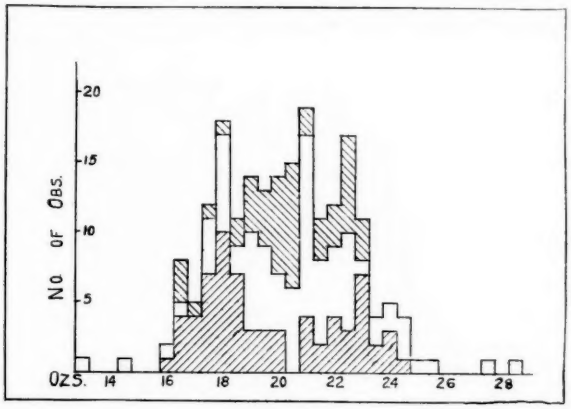


FIG. 11

tester, one lea test is said to have the statistical significance of only eight single-thread tests.

The usual rules call for twenty, thirty or fifty single thread tests as satisfactory for each sample of yarn, and no doubt these rules answer the purposes for which they are intended. The difficulty with yarn testing is this, and it applies to practically all kinds of yarns: that if samples are taken, say before and after treatment, there may be more variation inherent in the yarn than is caused by the treatment. Therefore, unless there is some sort of check on the regularity of the sample, the conclusions from a group of tests may be entirely wrong. Any high degree of tendering, for example, could be detected; but if it were desired to determine the influence of a series of processes on cotton, a step at a time, as in bleaching, it would be necessary to have a much closer control.

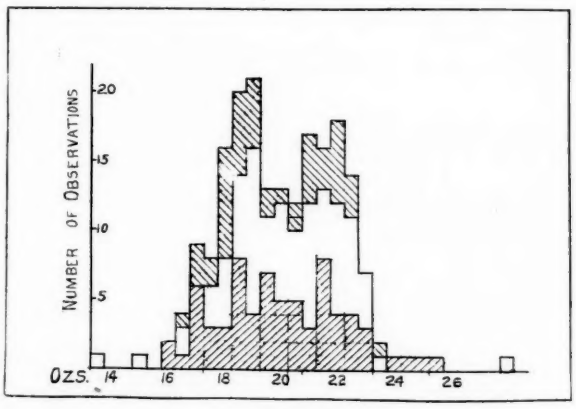


FIG. 12

As an example, we may consider two sections cut end to end from a wet warp of 378 "ends." One section was allowed to dry by mere exposure to the air, while the other was dried at a high temperature to see whether such drying had any deleterious effects. Since the two sections were joined together in the warp, they can be considered identical as near as it is possible to get ordinary yarns that will be identical. After hanging side by side in the laboratory for twenty-four hours after drying, 70 breaks were made from each, or about one-fifth of the total number of ends in each section of warp, and this would seem like a fair sample. Now the variation in textile materials follows somewhat the laws of chance just as does the variation of the length of the ears of corn from a plot of ground. There are various laws of statistics that are applied to the study of such natural phenomena, and they are applicable to some textile problems. Without going deeply into the subject, it can be

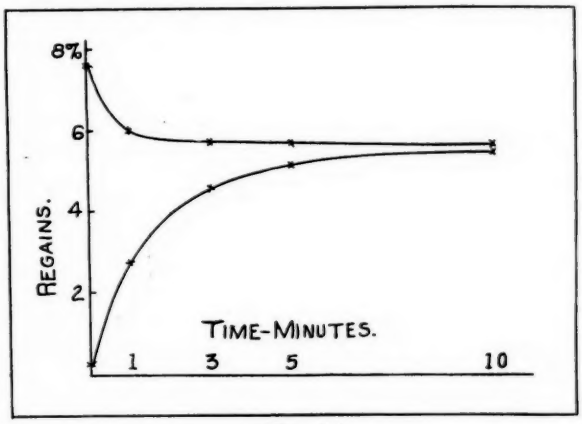


FIG. 13

said that materials free to vary in what may be called a natural way will follow the probability curve, if a sufficient sample is taken to truly represent the material. A typical curve of this sort is shown in Fig. 10.

Therefore, a simple test to see how nearly a sample has met the requirements, taken in conjunction with the known history of the sample, will give one a fair idea whether his result is reasonably correct.

Setting down the first seventy results in each case in a manner which is self-explanatory, as shown in Figs. 11 and 12, it is seen that the data are quite scattering and that there is no approach to a probability curve. For this reason, an additional eighty tests were run on each sample, the new results being added to the first, as shown without the cross hatching. Taking Fig. 11, it is still seen to be far from the characteristic form; and instead of varying around one average value it varies about 2 maxima, as though there might be two kinds of yarn in the warp.

Then another fifty tests were made on each, the threads all drawn at random as usual, and that was found sufficient to give curves of fairly satisfactory shape, although Fig. 12 now suggests two kinds of yarn.

While it would not seem necessary, 200 ends were broken from each warp, or over half the threads in it, in order to get results which could reasonably be regarded as comparative.

The results were as follows:

	Strength	Elongation	Regain
Air-dried	1.266 lbs.	4.44%	6.00%
Oven-dried	1.246	4.17	4.90
Difference absolute ..	0.020	0.27	1.10
Difference relative ..	1.600	6.10	...

If a greater difference had been expected between the two yarns and the accuracy requirement had not been so exacting, fewer tests would have answered the purpose.

Theoretically these two samples of the same yarn might have contained traces of mineral acid, and a weakening would have been expected in the one that was hot-dried. Actually it came out a trifle weaker, but consider that there is a higher regain for the air-dried than for the oven-dried. This alone might more than account for the difference, because each 1 per cent regain, between the limits of about 3 to 9 per cent, adds from 3 to 7 per cent to the strength of the goods. The figure depends greatly upon the construction of the yarn or fabric, but is accepted by the American Society for Testing Materials as about 6 per cent for ordinary yarns.

The lesson to be drawn from this portion of the experiment is that conditioning yarn may give a comparative basis in one sense but not necessarily in all respects. If one merely wants to know whether there is any practical difference between samples under the ordinary conditions of use, testing at air condition without reference to the exact moisture contents may be sufficient. For more scientific work, where the influence of each factor must be checked through to the final result, the moisture determination must be made, and, as in the present case, it may reverse the result, although for practical purposes it may be said not to

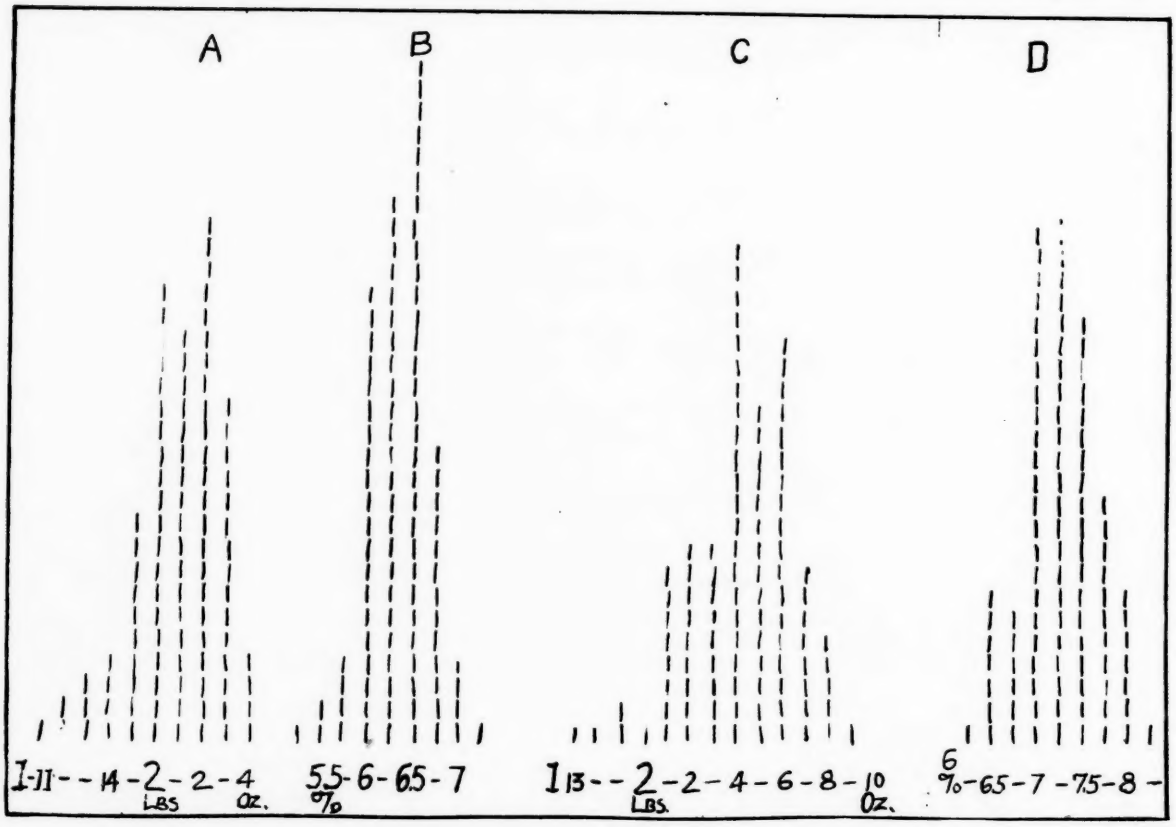


FIG. 14

make much difference in the usefulness of the conclusion—that there was no practical difference in the strength due to the method of drying. Even with all the precautions, the result was not very conclusive.

In order to overcome the effects of irregularities in the moisture content of samples, it is sometimes recommended to expose them under some specified conditions in a humidified chamber, and at the proper time to remove them and test quickly. The method has been tested and evidently found satisfactory for some purposes. A simple modification of it is to prepare desiccators with diluted sulphuric acid of such strength and vapor pressure as to give an atmosphere of the desired relative humidity, to put the samples in the desiccator for the necessary length of time for them to acquire the corresponding regain, then remove and make the tests.

Such a procedure should not be accepted on faith, but should be checked very carefully if the samples are to be tested at an atmospheric humidity very different from the relative humidity in the desiccator. As evidence that this factor may become quite important, the writer has observed relative humidities in laboratories under perfectly natural conditions, varying from 20 per cent to over 80 per cent. That this may have a serious influence is shown by Fig. 13, which shows the behavior of small skeins of yarn that were conditioned to contain the amounts of moisture shown at the intersections of the curves with the chart axis. One of them was practically bone-dry, while the other was halfway between the accepted standard regain of 8½ per cent and the regain of 6½ per cent, which is frequently considered a standard in testing laboratories. They were transferred to an atmosphere of about 4 per cent relative humidity, freely exposed for one minute, weighed without further change of moisture, then further exposed for the intervals indicated, and weighed each time. The curves show the moisture gains and losses, which are summarized below:

Total Exposure (minutes)	Regain at Time Noted	Gain in Regain
0	0.28	...
1	2.69	2.41
3	4.62	4.34
5	5.13	4.85
10	5.45	5.17
		Loss in Regain
0	7.66	...
1	6.01	1.65
3	5.71	1.95
5	5.71	1.95
10	5.63	2.00

It can be seen that yarn starting a little below 8 per cent regain dropped in the first minute more than 1½ per cent and came almost to its equilibrium moisture. The bone-dry sample came nearly halfway to equilibrium in the first minute.

It is evident that this is another procedure that should be used with some discretion, and even more

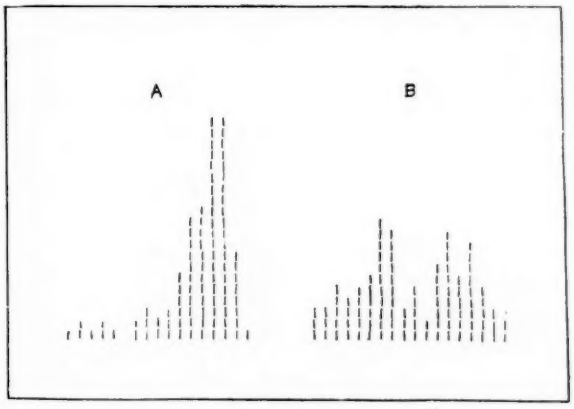


FIG. 15

care may be required if the attempt is made to test bone-dry samples in an ordinary atmosphere.

Coming back to yarn testing, it is, of course, not always necessary to make 200 tests on a single sample; but for most research purposes the writer has adopted 100 as being a safe number, although sometimes it is more than absolutely necessary. Characteristic diagrams for 100 breaks from single cones show that usually this number is required for accuracy. Figs. 14 and 15 are drawn free-hand just as they would be made in the laboratory.

In Fig. 14, A and B show the values of breaking strength and elongation-at-break for a 40/2 cotton yarn at about 66 per cent relative humidity (6.76 per cent regain); C and D are similar data for the same cone of yarn at 9.73 per cent regain, tested at about 82 per cent relative humidity. For completeness, the average values obtained are given as follows:

	Breaking Strength	Elongation-at-Break
At 66% relative humidity	2.05 lbs.	6.34%
At 82% relative humidity	2.28	7.27
Difference, absolute	0.23	0.93
Difference, relative	11.20	14.70

In this particular instance, for each per cent regain there is a difference of nearly 4 per cent in strength and nearly 5 per cent in elongation-at-break.

Fig. 15, A shows a one-sided diagram and B a double

diagram, both for breaking strength. These were supposed to be comparative from the same cone but neither is very satisfactory. In B the average comes in the middle, where very few actual observations were recorded.

Correction for Weight of Yarn

The writer has sometimes applied another correction to the results of tensile strength tests. In raw silk testing it is customary to express the strength of the silk in grams per denier, thus furnishing a figure for the strength or quality of the silk substance uninfluenced by variations in size. Similarly in testing cotton yarns, better comparative results may be obtained by taking into account differences in the bone-dry weights of the samples. This applies only where there is exact similarity in the yarns, except for some slight accidental variation in size, or where the strength is a function of cotton substance rather than of yarn structure, or of modification in its structure by some treatment. In one instance a series of tensile strength tests gave:

Experiment No.	Breaking Strength
1	161.2
3	160.0
5	151.2
7	150.0

There was no apparent consistency between these figures and the conditions of the experiments. On taking into account the bone-dry weights referred to the No. 3 as a standard, the figures became 167, 160, 155, 152, which were in the order to be expected. These were lea tests, averages of only 5 breaks, and were thus put upon the basis of yarn properties uninfluenced by slight accidental variations in yarn size.

Elastic Properties of Yarns

The elongation at the break is frequently called elasticity and taken as a measure of the elastic properties of a yarn. It is not true elasticity, because, even if not broken, the yarn would not come back to its original

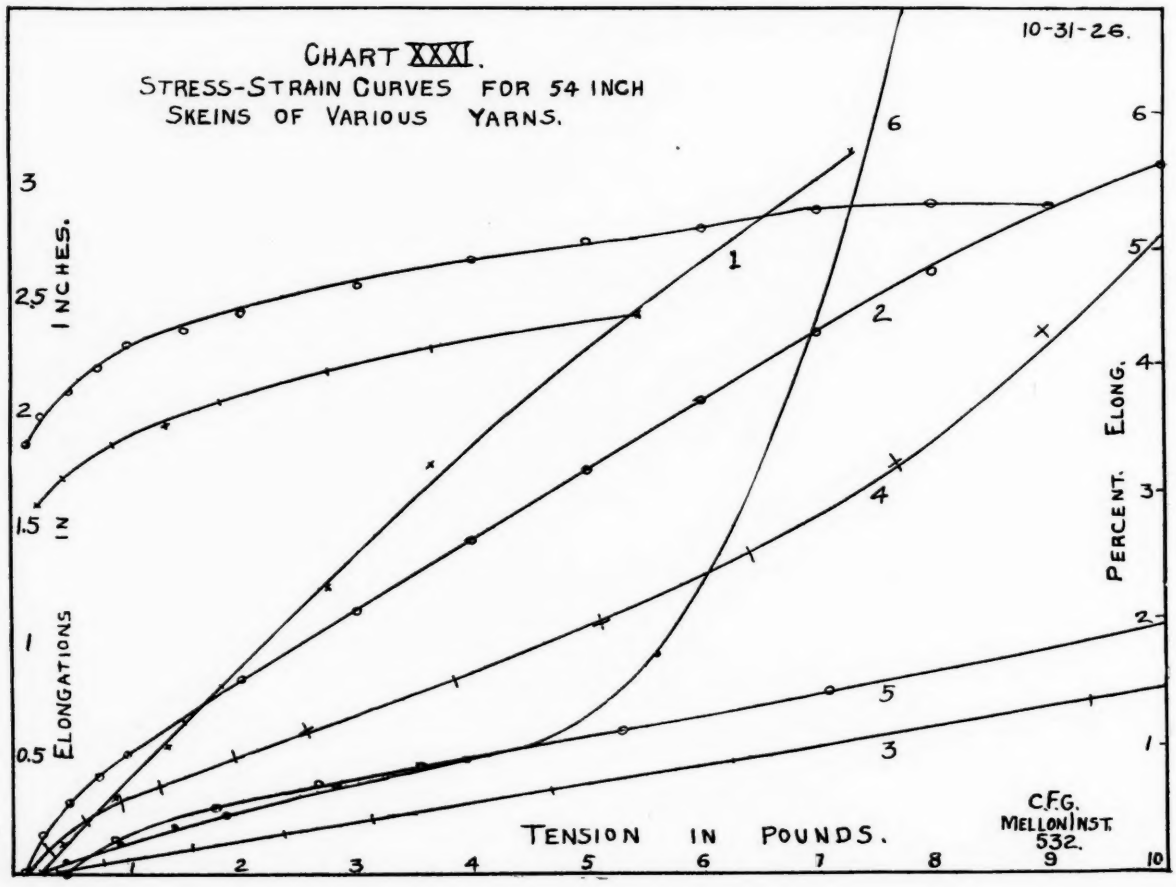


Fig. 16

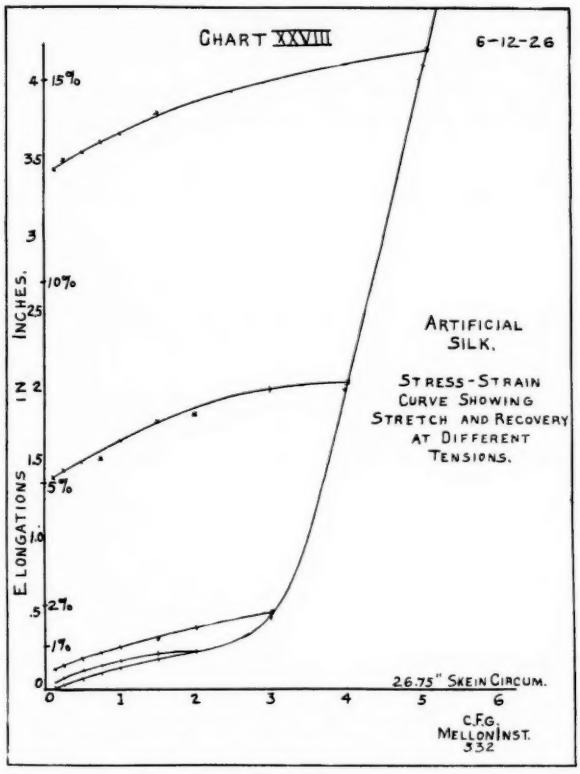


FIG. 17

length. Also, owing to the complex nature of the stretching operation, elongation at the break does not tell the whole story. Different kinds of yarn behave very differently, and a few characteristic curves are shown in Fig. 16 reduced to approximately comparative conditions.

Briefly, the curve for cotton yarn (2) is about the same as that already discussed in Fig. 1. The artificial silk curve (6) is characterized by a very regular and slow increase in length for the lighter loads, and a sudden giving way. This familiar type of curve strongly suggests plastic flow, where a minimum force is required before there is any corresponding motion and a change of shape.

By adding curves for the return as the stress is removed from the fiber, this curve becomes more interesting (see Fig. 17). Up to the pronounced bend the stretch approaches true elasticity, for the material will return to somewhere near its original length. Above the bend a large permanent elongation takes place, for, on unloading, the yarn does not come nearly back. The rayon has become finer and much more lustrous; in other words, it has become a "shiner."

Real silk has something of the property of the rayon, but the silk is so much stronger that the curve does not all come within the diagram. There is a similar drawing-out effect, which may appear in winding soaked silk. A dry skein that is partly run out will wind off at a low tension, while a full-sized skein heavy with soaking liquor will drag, require more tension, and stretch the silk. Cockly and corkscrew effects sometimes originate from this cause, as the silk stretched to different degrees does not return uniformly.

Thrown silk in the form of a thread (5) is made of continuous fibers that run through its whole length. The shape of its curve at the lower end, as contrasted with that for the raw silk that has no twist, is due to the tightening up of the twist and the tendency for the single yarns to straighten, the same as in cotton but without the complication of slipping fibers. Crepe, with a higher twist, shows the effect to a proportionately greater extent (4).

The wool fiber taken separately has a curve that resembles those for silk and rayon, while its yarn made up from many fibers shows something of the cotton yarn characteristics.

There are elastic after-effects and slow returns to more nearly the original lengths that are not shown in these relatively simple experiments. Wool can actually be stretched up to 70 per cent if damp, and will in time return to its original length, according to recent work by Speakman. Under ordinary conditions it has something of the same property, and that is said to be the reason that a wool suit lain away for a time will be found to look better when it is taken out again. The baggy knees, strained elbows and vanishing creases have come back to some extent. Storage, however, has not yet become an accepted substitute for the tailor.

Just as the stress-strain curves show the great differences between the elastic properties of yarns made from different fibers, they will also show differences that may be due to physical or chemical treatment.

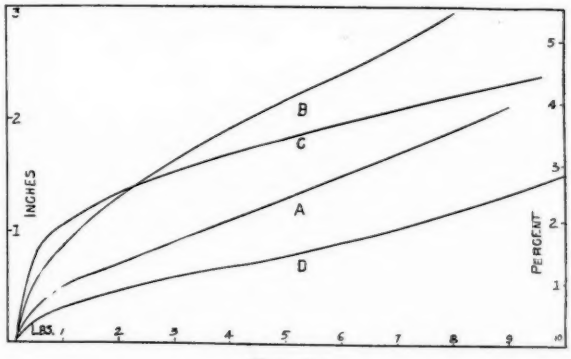


FIG. 18

Fig. 18 shows a group of cotton yarns, where curve C represents a yarn taken from a stocking in which the crimp due to the loops had been "set" by the dyeing and finishing operations. It all came out at the beginning of the curve before the other effects appeared to any notable extent. Curve A is for a normal two-ply cotton yarn, while B is for the same yarn simply wet-out as it might be for skein dyeing, and dried without any tension. Curve D represents a similar yarn that has been warp mercerized and therefore subjected to tension. It has been found by a large number of experiments that the past history may be very clearly reflected in the stress-strain curves, and the method is suggested for use where complete knowledge is desired of the effects of any process.

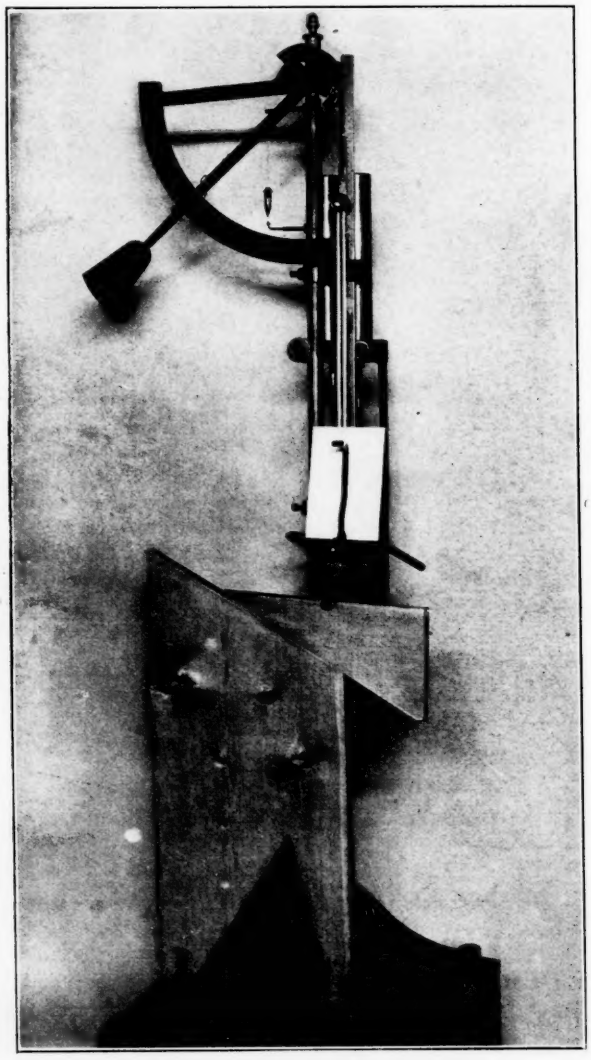


FIG. 19

Such curves can be made by any device that will allow loads to be applied and corresponding elongations to be measured. Machines can be purchased which will automatically give a continuous curve; and while this method of charting seems to be favored by most of the British workers, it does not seem necessary for ordinary comparative results. The writer's results have been obtained by different methods, but very largely with a modified Baer single-thread tester. This familiar type of machine was used simply because it was available. As shown in Fig. 19, sliding wedges of board were arranged to arrest the motion of the falling weight at any desired position, and extra hooks were applied to take skeins of the full length as found on the 54-inch wrap reel, or to take such skeins doubled. Elongations are recorded as units of length instead of a percentage. Small skeins of 6 full turns, or 12 ends between supports, have been found just right for 40/2 coton yarn, but the amounts of materials have to be varied to keep within the capacity of the machine.

The figures and curves given throughout this paper have been chosen as illustrations rather than for any general significance that they may have, for the intention has been to discuss principles rather than to present definite research results. It is believed that a greater appreciation of the importance of such details will help eliminate the inconsistencies and unsatisfactory results that are so frequently encountered in textile experiments. It is hoped, too, that some useful methods of treatment have been suggested.

Chairman Killheffer—If there is no discussion on this paper we will proceed immediately to the next paper, "Modern Theories of Dyeing," by Dr. R. E. Rose. (Applause.)

Modern Theories of Dyeing

By Dr. R. E. Rose
E. I. du Pont de Nemours & Co.

The effort to find an explanation for the facts of dyeing is a consequence of our inherent pleasure in trying to explain what we see. Theories of dyeing have come to the front as we have realized that theories in general help us to understand the nature of facts and lead us to a better control of processes or, in other words, basic knowledge makes art more successful. Dyeing used to be so menial a job that nobody tried to explain it. It wasn't thought worthy of such an effort; but when the scientific type of man arose this state of affairs changed since the scientist considers nothing menial; all facts are equally worthy in his sight.

Early Theory

In those early days dyeing was effected chiefly by the use of mordants and a very simple theory arose with which to explain the facts. It was that the fiber was opened up by the mordanting and then the cracks, as it were, were sealed up in the subsequent proceeding so that the dyestuff got caught inside the fiber. The first theory, then, was mechanical. With the coming of the artificial colors a lot more investigation was carried out and many facts were found which refused to admit of such a simple mechanical interpretation. Three theories of dyeing were then advanced:

a. Chemical—An actual compound is formed between the dyestuff and the fiber.

b. Mechanical—The dyestuff is deposited upon the fiber by what the physical chemist calls adsorption.

c. Physical—The dyestuff is dissolved in the fiber as a solid solution.

These theories were upheld by their representative protagonists, each of whom adduced a great deal of evidence which favored his own pet interpretation, but, as in all such cases, the contender for the opposing theory was very often able to show that the facts might be interpreted exactly the opposite way.

The Dyestuff in Solution

At this stage let us stop for a moment to consider the possibilities before us. Let us forget dyeing for the moment and simply consider a dyestuff in solution. The dyestuff in solution presumably is like any other body in solution. At the end of the dyeing operation it is out of solution. Now, without considering the fiber, how is it that a substance can be taken out of solution? To answer this question we have but to refer to the simple processes of inorganic chemistry. A substance may be removed from solution:

a. By precipitation, that is, by causing it to combine with some other material which robs it of its solubility in the solvent. Usually the precipitation carries down only part of the substance, for instance, the precipitation of barium, as barium sulphate would leave an acid radical previously combined with the barium in the solution.

b. The substance may be removed by driving it off in the form of gas, as ammonia can be distilled from water.

c. The substance can be precipitated by adding another liquid to the solvent in which the substance dissolved is not itself soluble. For instance, we can precipitate copper sulphate from water solution by the addition of alcohol.

d. A substance can be removed by dissolving it in a liquid not soluble in the solvent, but into which the dissolved material passes. For instance, we may extract an alkaloid from a water solution by shaking with chloroform.

e. The dissolved material can be precipitated by what is known as adsorption. This is what happens when animal charcoal is used to decolorize sugar.

f. Finally, the substance may be precipitated by removing the solvent, it being left behind if it is not volatile.

Let us consider the dyestuff solution; we have to remember the possibilities by which the dye can be removed as we see it removed during the dyeing operation. However, of the possibilities some are excluded at once. We do not precipitate the dyestuff by the addition of another liquid, nor do we precipitate it by removing the solvent; nor do we drive it off in the form of vapor. We cause it to precipitate inasmuch as it is precipitated by adding a fiber. Now, a fiber may act as does barium chloride when it is added to sulphuric acid; it is at least possible to think of it in this way. Or it may act as animal charcoal does and take up the coloring matter, but there seems no reason why it should not also act as an immiscible material in which the dyestuff is soluble and extract it from solution as chloroform or ether might remove some solutes.

Three Theories of Dyeing

We come then to exactly the three theories which have been propounded. A chemical precipitation, adsorption, or solution. What is the evidence? I don't want to bother you with it. There has been such a tremendous amount of it collected. I prefer rather to pick out a few facts and let them carry their own meaning to you. The earliest attempt at chemical explanation was that involving the dyeing of wool by means of Magenta. Knecht was able to show that when Magenta dyes wool the acid of the Magenta, because Magenta is a salt, remained in the solution and the positive radical of the dyestuff went into the wool. This is exactly analogous to what happened when we added barium chloride to sulphuric acid The opponents of this theory were able to show that the Magenta could be extracted by using alcohol and that there really was very slight evidence for saying that we were dealing with a real chemical compound. However, the opponents were not so very strong in the case of the dyeing of wool because wool is essentially a basic material which ought to be rather reactive and therefore it would not be surprising if some kind of chemical reaction were involved.

Turning to cotton the opponents of the chemical theory had a much better case. They argued that cotton was chemically inert; that the dyestuff itself was precipitated on the fiber as a sodium salt; that the dyestuff was colloidal and that the colloidal particles of the typical cotton dyestuff are positive while cotton itself is negatively charged as against water. They pointed out that the

difference in electric charge would cause the first precipitation on the fiber; that once on the fiber there would be a tendency for the extremely fine particles to agglomerate. However, there was also a tendency to come off because dyeings with direct colors are reversible in the sense that they bleed into water or onto neighboring fibers.

Witte was the only strong upholder of the third alternative. He argued that dyeing, as a rule, came of solution, and that the dyestuff passed into the fiber where it was held simply because it was more soluble in the fiber than it was in the water about it. This theory was never received with much enthusiasm, and a great many of the facts do actually contradict it so flatly that we may regard it as more or less abandoned except for the limited extent to which I shall refer later.

The Adsorption Theory

The adsorption theory requires that the dyes in solution should actually be colloidal. Now that is something which can be proved easily and all the physical chemical work done goes to show that at least the cotton colors are partially under the conditions of the dye bath, in a highly dispersed colloidal state. They are so highly dispersed that there are a great many particles present in a constant state of movement, known as Brownian movement; that is, the particles are so small that they are jostled and pushed and rolled around by the molecules of the solvent. The degree of dispersion is increased by heating. It is decreased by the addition of mineral salts. What other evidence is there in favor of this theory? If we take a dye which is very highly dispersed then it ought to be on the verge of being too highly dispersed to dye cotton. If we take a dyestuff which is too coarse we might easily push it below the degree of fineness necessary for dyeing, and this all without making the solution look much different.

The best evidence in this connection is to consider the case of wool and cotton together. The proponents of the adsorption theory are not willing to admit that wool is in a different class, and they claim that the dyeing of wool is simply another phase of the same process. A very neat piece of work which lends itself to this argument is one carried out by Haller, who took pigments such as Indigo Blue (unreduced), Alizarine Red, Para Red and Indanthrene Blue and shook them up with cotton and with wool. He found that the cotton was stained rather more than one would expect by mere chance contact with the pigment, but that the union between the pigment particles and the cotton was extremely loose, so loose that the particles could be washed off very largely by cold water and completely by hot water with some soap. Wool, however, took up the pigments much more firmly. Indigo, for instance, dyed the wool very feebly but still sufficiently to speak of a dyeing, and it retained the color even when efforts were made to wash off the pigment. Under the microscope the condition in the case of the cotton was quite obviously that of coarse particles distributed unevenly over the surface.

In the case of the wool the fiber looked almost homogeneously colored, although there were little granulations here and there. Haller argued that there could not possibly be any question of chemical action between such inert pigments and wool, therefore he claimed to prove that wool and cotton dye in the same way. That being so, he went on to generalize and stated that those colors which dye cotton are less finely divided than those which dye wool. He was able to show that this is true by physical chemical methods. He argued from this point that it might quite well be that we could so influence the degree of dispersion of a dye as to make it at one moment a wool dye and at the next a cotton dye.

He based his statement on the fact that the dyestuff is characteristically what the colloid chemist calls a poly disperse phase system which is temperature sensitive; or, in plain English, a dyestuff in solution floats as particles of various sizes from those little bigger than molecules to comparatively coarse clumps, and changes in temperature alter the average size of the particles. A rising temperature promotes fineness of division; therefore, said Haller, if we take a dyestuff which is a cotton dye at ordinary temperatures and leaves wool white, and boil it, it ought to dye wool and cotton to the same extent or perhaps it may dye wool deeper than the cotton. Now, of course, this is exactly what every union dyer knows to take place, but no union dyer has checked up cold dyeing union colors to find out how disperse they are. Haller did this and the actual physical measurements confirmed his theory very nicely.

What Is the Fiber Surface?

I think we can say that the adsorption theory of dyeing is the most generally accepted at present, but it still fails to explain all the facts, perhaps simply because we do not know the facts well enough. Adsorption refers to the surface of the fiber, but we must not confuse the surface in the ordinary sense of the word with that available for dyeing. At least, that is my present view of the case, and I should like to see a great deal more work done in elucidating this problem on fibers whose structure we are able to control.

I think if the investigator of problems of dyeing would turn to artificial fibers he might derive great benefit from doing so. Let me illustrate my point. All of you who have handled the dyeing of rayon are familiar with one of its most offensive characteristics from the dyer's point of view, namely, that it is extremely apt to dye unevenly,

not in the ordinary sense of an uneven wool dyeing, but in the sense of uneven portions. For instance, half a skein may possibly come out 20 per cent deeper than the other half—that is an extreme case and rare now that the rayon companies check up on this point; but it is yet impossible to dye rayon-faced piece goods owing to the practical certainty that the skeins used in the weaving differed. Why is this so? We do not know definitely, but these facts stand out: If we take two samples of the same rayon and examine the filament by making cross sections we may find that one has a more irregular outline than the other; one is more shrunken and withered, as it were, the other rounder and fuller.

If we do find this we will also find that the more shrunken fiber dyes to a deeper shade. This, of course, is exactly what we would expect from the adsorption theory. The surface of the shrunken fiber is greater; gives more reflections and actually more dyestuff goes on, but we may take two samples of dissimilar rayon which, on cross section, are found to be identical mechanically, and on dyeing them up find that one dyes much darker than the other. How is this to be interpreted? For instance, to give it its most extreme form, cuprammonium silk is a perfectly straight fiber without any wrinkles, but it dyes much deeper than viscose. Perhaps there is a difference in chemical composition. If we investigate this we find that such difference as exists is in favor of the cuprammonium not dyeing as dark as the viscose silk, so that this argument is not sufficient.

Now, if you will allow me a guess, it is that the specific gravity of cuprammonium silk is less than that of viscose silk, disregarding the moisture present in the two fibers. That is, the actual substance of the cuprammonium filament, although it is round, occupies more space for a given weight than does the filament of the viscose silk and that leads me to believe that in dyeing we must regard the available surface as a good deal more than the mere outer edge of a microscopic cross section, and this although the dye may not apparently progress very far into the interior of the filament.

Study Needed on Acetyl Cellulose

I should like to see work done on acetyl cellulose because that is fundamentally different from viscose and we know that when it is dyed with basic colors we get a film; that is to say, the dyeing is comparable to that of cotton. When we dye acetyl cellulose with those colors especially manufactured for this purpose, we are dealing with a case of true solution; that is to say, we have here what Witte argued we must have in all cases. All those who have investigated this point agree to this. If that is so, I feel that dyeing in other cases may not be altogether adsorption. I am coming rather to agree with Georgevics, who insisted that there was a certain amount of color dissolved before adsorption took place. I am inclined to interpret Haller's work on dyeing wool with unreduced pigment dyestuffs as being a case of solution in the fiber.

Perhaps you will say that all of this is very pleasing, but it doesn't help the dyer in the dyehouse. I think that it does. It always helps to understand more clearly what one is doing. If you appreciate that when you raise the temperature in dyeing unions you are increasing the dispersion of the dyestuff, thereby favoring the wool, or if you understand that the addition of sulphuric acid causes an increase in the positive charge owing to the adsorption of positive ions, which in turn enables the wool fiber to take up the negative particles of the dyestuff, this also helps you to reason rather than to act merely as a machine. In the case of cotton dyeing the principal effect of the addition of salt is to decrease the degree of dispersion. This can, of course, result in the precipitation of the dyestuff, but if it is properly controlled it will keep the dispersion at the point at which the dyeing is most effectively carried out.

Finally, if you understand that the dyestuff, when it is adsorbed on the fiber, is still capable of being moved and grouped in coarser aggregates, you will appreciate something definite about the results of soaping because, during soaping, as microphotographs show, pigment colors, like the Naphthol AS colors, and some of the vat colors, actually move on the fiber and group themselves in larger clusters and these larger particles resist washing; and, moreover, they resist light distinctly better than the finer particles. The conversion of the small into the larger particles is always accompanied by a change in hue to a greater or lesser extent.

To me it is these considerations that make of the dyehouse an experimental laboratory of great interest instead of a place where there is nothing but dull, routine work. I am not employed in a dyehouse and probably if I were I would not last long because I would try some experiment that would be extremely interesting but extremely painful to the management in their desire to produce passable goods.

Chairman Killheffer—Is there any discussion on Dr. Rose's paper?

Allan A. Claflin—I should like to call the attention of the Association and Dr. Rose to the very interesting work that Dr. Clarke of the X-Ray Laboratory of Technology is doing on the theory, and say that one trouble perhaps about the work on artificial fibers is that it has been shown by the X-ray work that in natural fibers we have more of an orderly arrangement of the atoms, a more exact orientation, as they express it which keeps them more systematic, more symmetrical substances than we get in the artificial fibers. Whether you consider it

a chemical combination or adsorption (if there is a distinction between them) I think that Dr. Clarke has shown in his book, which will be published quite shortly, that there is a distinct location of the dyestuff molecules, if you use the term (I believe they don't admit there are any molecules now), that the dyestuffs, themselves, are distinctly placed around the atoms or molecules of the fiber, and that the X-ray point of attack is going to clear up the whole thing.

Chairman Killheffer—Is there any further discussion on this paper? If not, we will pass to the next paper. "Vat Dye Development in America," by Mr. Stott.

. . . Mr. Stott then presented his prepared paper.

The Development of Vat Colors in America

By P. H. Stott
Newport Chemical Works, Inc.

The twenty-five years which have passed since the first vat color of the anthraquinone series was discovered have naturally been devoted, in all circles interested in the development of these colors, to a great amount of research. This has been centered along the lines of both new dyestuffs and new uses for them. This association has, since its inception, contributed its share of valuable information in the application of these, the fastest of all known dyestuffs, to various fibers. There are unquestionably present to-day in this meeting, many who have studied these colors from a special standpoint and whose information has probably never been published. Whether or not this knowledge is personal or public, it must be regarded as a great asset to the textile industry for, as I shall attempt to show you by figures, the demand for faster colors is increasing and consequently any new applications of such colors must be regarded as progress.

Divisions of Subject

I have been asked to speak to you on the "Development of Vat Colors in America." In the face of what has already been accomplished it would be presumptuous, indeed, were I to attempt to describe the entire history of their application in this country. It is well known that American textile chemists were among the first to successfully use these colors in the pad and on the jig. I can probably give you no new information on this or on the dyeing of either raw cotton or yarn. Probably the most lucrative field of research has been the dyeing of viscose, for which these colors are admirably suited. Their application to pure silk, particularly in the piece, presents a further field for development.

If, therefore, you will bear with me, I would like to divide this paper into two parts:

1. To trace, as briefly as is consistent with the importance of the subject, the development of American-made vat dyes to the present time, and
2. To outline future possibilities in production and application, if for no other purpose than to suggest possible fields for further practical research.

What Is a Vat Color?

While it may seem unnecessary, let us first of all define what is meant by the term "vat color." As a matter of actual fact, vat colors have been known to man since what we are pleased to term "prehistoric times." They took their name from a process of fermentation of natural plants, roots, etc., which, by this process, could be converted into coloring matters. This fermentation was conducted in large wooden "vats," and the name has been adopted by modern dye chemists because Indigo was one of the products of this fermentation process and, therefore, is probably the oldest known vat color. Modern chemistry has done away, practically altogether, with both natural Indigo and the fermentation vat and has supplanted the former by synthetic Indigo, and the latter by a reduction medium—sodium hydrosulphite. This compound, and its derivatives, in the presence of alkali has the power of converting the otherwise insoluble Indigo, into its so-called leuco derivative, in which form it has affinity for both vegetable and animal fiber. Other dyestuffs, then, which possess this characteristic, have come to be known as vat colors, and the modern definition of such a color is one which is insoluble in water and dilute acids and alkalies, but which, when reduced in alkaline solution, changes to its leuco form, and in this condition is soluble and substantive to vegetable and animal fibers.

Synthetic Indigo was first made in 1882 by Bayer and the process was developed commercially as we all know. Vat dyestuffs other than Indigo were first produced in 1901 by Bohn.

What we to-day regard as vat colors are not necessarily of similar chemical constitution to Indigo. They can be devided into two main classes:

1. The Anthraquinones.
2. The Indigoids

From their inception in 1901, until 1914, various brands of German or Swiss origin made their appearance under the names Indanthrene, Algol, Hydron, Helindone, Thio-Indigo and Cibanone. In the fiscal year 1913-1914, fifty-eight different colors of the anthraquinone class, and thirty-six of the indigoid class, were imported into this country, in amounts of about 1¾ million pounds of the former, and rather over 300,000 pounds of the latter, exclusive of Indigo itself.

I can give you some of the figures of the more important:

	Pounds
Indigo	8,507,359
Indanthrene Blue GCD	478,980
Indanthrene Blue RS	187,379
Indanthrene Yellow G	75,192
Indanthrene Green B	72,227
Indanthrene Violet RR	68,419
Indanthrene Golden Orange R	50,496
Indanthrene Black B	50,034

So we see at once that American dyers realized the possibilities of these colors and, with the outbreak of war in 1914 and the resultant well-remembered dyestuff famine in this country, the lack was felt at once, along with all other classes of dyestuffs and caused the birth of the American vat dye industry. At the outset, efforts were directed toward increasing the production of direct, acid and sulphur colors, which has previously been made on a more or less limited scale. The reasons for this, of course, are not hard to find. Some of the more important basic ones were:

1. To supply the consuming trade with colors which were important as to bulk.

2. To utilize to the fullest possible advantage the available raw materials and scientific knowledge.

The achievement of these two things alone in a comparatively short space of time, represented a remarkable scientific triumph for America; but yet, while they were gradually being accomplished, plants were being built, technical organizations carefully selected and trained, and upon the very fragile structure of German patent literature, scientific investigation was being started in a hitherto untouched field—that of vat dyestuffs. The difficulties encountered were sufficient to discourage the most optimistic. In addition to the lack of correct scientific data referred to above, the ghost of lack of raw material presented itself with an ominous gesture.

Early Research on Vats

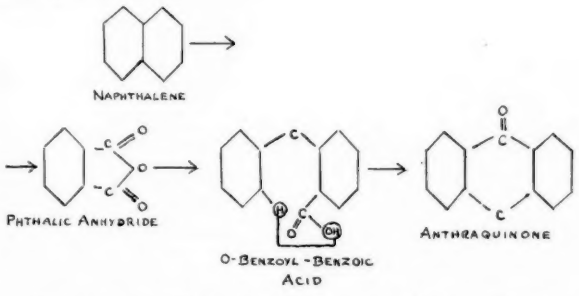
In the chemical research work it was necessary to start at the very bottom and study the fundamental principles underlying the chemistry of anthracene and anthraquinone. As the name implies, the latter is the starting point, or base intermediate for vat colors of the anthraquinone series, to which belong Blue GCD, Yellow G, etc. Anthraquinone is made by the oxidation of anthracene, a raw material present in coal tar.

In the fractional distillation of coal tar there are four main fractions, which are classified by their boiling points:

1. Light oil	Up to 170 deg. Cent.
2. Middle oils	170 to 230 deg. Cent.
3. Heavy oils	230 to 270 deg. Cent.
4. Anthracene oils	270 to 400 deg. Cent.

The question of economy of operation enters here, as the pitch left as residue of the distillation cannot be successfully used for road making if all the anthracene is extracted. Therefore, it lost much of its value as a by-product, and the anthracene had to stand the cost. This, coupled with the fact that there was no American production of pyridine, which is the extracting solvent for anthracene, made matters very unsatisfactory from a standpoint of cost of raw material.

Thanks, however, to the invaluable work performed by the Government chemical staff in 1917, it was discovered that naphthalene vapors could be changed into phthalic anhydride by suitable catalysts. This admitted of the making of anthraquinone by the condensation of phthalic anhydride with benzene to o-benzoyl-benzoic acid. By splitting off water from this, one arrives at synthetic anthraquinone. The chemical reactions governing these changes are as follows:



From here on the actual problem of the dyestuffs themselves presented itself. Or, I should say, each individual dyestuff presented itself as an individual problem. I have not time to enter into a technical discussion of the difficulties encountered and the problems solved, but rather let me here pay a tribute to the chemists and engineers who overcame the old, and are still attacking the new difficulties. Just as actual dyehouse problems are not entirely solved in the beakers of the laboratory, so are the manufacturing problems of vat colors quite different from the same problems encountered in the laboratory.

Manufacturing Difficulties

Apparatus which must resist the action of powerful chemicals at temperatures of 200 deg. Cent. and pressures of 800 pounds per square inch, had to be designed and constructed. Innumerable difficulties of filtration, evaporation and separation presented themselves, but by patience, perseverance and skill these were gradually

overcome, and as early as 1919 the first American-made anthraquinone dyestuff was produced. As you all know, these colors appear on the market as Anthrene Colors made by the Newport Chemical Works, and Ponsol Colors made by the Du Pont Company, which are the two main producers. On August 15, 1920, the Newport Chemical Works introduced Anthrene Dark Blue BO, quickly followed by Anthrene Blue GCD and RS, Green B, Brown BB and Yellow G. The year 1922 saw the introduction of Anthrene Jade Green, unique in its position of being the brightest vat green ever produced, and significant in the fact that it has no German prototype. This, indeed, was a most signal triumph for the creative ability of American chemists. Realizing the necessity for a complete line, both manufacturers continued to introduce additions to the anthraquinone line, and then turned their attention to the indigoid group. The tabulation of colors as produced by years, is as follows. This includes both manufacturers.

	Schultz No.	Colour Index No.
1919		
Blue GCD	842	1113
Yellow G	849	1118
Dark Blue BO	763	1099
Green B	765	1102
Violet R	766	1103
1920		
Blue RS	837	1106
Violet RR	767	1104
Brown B	867	1120
1922		
Jade Green	...	1101
Blue GC	843	1115
Blue BCS	...	1114
1923		
Golden Orange G	760	1096
Blue 3G	840	1109
*Pink FF	...	...
1924		
Golden Orange RRT	...	...
Golden Orange 4R	...	...
Red BN	831	1162
*Orange R	...	...
Blue G	...	...
*Scarlet 2B	...	...
1925		
Red Violet RRN	871	1161
1926		
Pink B	...	...
*Pink FB	...	...
*Brilliant Red 3B	...	...
Violet RN	832	1163
*Violet B	...	...
*Violet R	...	...

*Indigoids.

Definite proof of the demand for faster and better colors by the public, and a desire on the part of dye users and manufacturers to supply them is shown by figures (covering vat dyes only) taken from the Dye Census of the U. S. Tariff Commission for the years 1914-1925, inclusive. These figures do not include Indigo.

Year	Production	Imports
1914	.....	1,945,304
1917	14,525	.....
1918	197,449	.....
1919	389,158	.....
1920	1,159,868	761,363
1921	345,152	1,045,370
1922	1,075,992	1,548,519
1923	1,766,383	1,207,554
1924	1,821,319	1,493,851
1925	2,608,361	2,416,890

We thus see that American production in 1925 exceeded the total importations in 1914 or any succeeding year. This is most convincing proof of the good-will and enterprise of the American manufacturers. The quality of his products is as good as European products, and in some cases better. The line is rapidly being increased and will, with the support of attendant industries, soon reach a point when America will be as independent of imported vat colors as she is to-day of imported direct, acid and sulphur colors. The close and confident co-operation necessary to the success of any new enterprise, must be given by all concerned. We must support, to the utmost of our ability, our own professional skill; we must look continually for avenues of progress and development in all branches of the industry; we must seek to create, as well as imitate. Basing our thoughts always on the fundamental desire for conquest and success, then let us with all means at our command, meet the increasing demand for faster colors by developing the uses of these colors, knowing that such development will receive the heartiest co-operation of the manufacturers, and encourage further additions to an already very complete line of American-made vat colors.

Vat Colors for Silk

I have with me a number of dyeings on various fibers made by various methods which are intended to illustrate what can be done with vat colors, and I shall refer to these in this, the second half of this paper.

It probably is not necessary to say much about the application of vat colors to cotton. On July 18, 1925, M. Mackenzie read a paper before the Southern Section which dealt at some length with application. At the last annual meeting, F. Warshaw presented a paper on the dyeing of rayon, and there have been several others at various times. For purposes of illustration, therefore, you will find in the collection of dyeings referred to:

1. Dyeings made in the Franklin machine on cotton yarn.
2. Piece goods—cotton.
3. Dyeings on viscose twist.
4. Prints and colored discharge prints on cotton.

What I more particularly wish to do this afternoon is to submit for your consideration some experimental data which led us to investigate the practicability of dyeing vat colors on pure silk piece goods.

The latest development in the manufacture of vat colors is the recent introduction of the so-called Indigosol colors. These dyestuffs are derivatives of vat colors, but, as distinct from vat colors themselves, are soluble in water without caustic soda, and in this form are substantive to both vegetable and animal fibers. They undoubtedly have created a lot of interest, particularly among silk dyers. At present, however, they are not only high in cost, but are relatively weak tinctorially, particularly on cotton. It is not in keeping with the established policy of "Newport" to bring its products to the attention of the consuming trade until such products are actually ready for distribution, but as I am speaking on the American development of the industry, I can state that we have made a number of soluble Anthrene Colors which have been called "Sol-Anthrene." As far as research has progressed, it appears that the process of making anthraquinone dyes in a soluble form is accompanied by considerable loss of tinctorial value. I have in my collection of dyeings silk crepe dyed on an experimental reel for purposes of illustration.

Our own opinion is that the regular anthraquinone and Indigoid dyes can, and will be, successfully dyed on silk without difficulty, and so obviate the necessity for the weaker and comparatively more expensive soluble vats.

While the dyeing of Celanese can not be done with vat colors, beautiful effects can be produced in a Celanese-cotton mixed fabric by dyeing the cotton with vats and cross dyeing the Celanese with colors suitable for this fiber, as most vat colors leave Celanese practically white. Again, while conflicting with our firm's policy as regards the announcement of new colors, and, therefore, only with a view of making this story of American development as complete and up to the minute as possible, I may say that we have now in preparation a series of so-called Cel-anthrene Colors. The name is self-explanatory. I have dyeings with me which will illustrate a few of these colors on cotton-Celanese goods; the cotton being dyed with Anthrenes and Thianthrenes.

Problem of Caustic Reduction

Just as soluble vats require no caustic soda, so must the quantity of this chemical be kept as low as possible in dyeing cotton-Celanese mixed goods to avoid partial saponification and loss in luster. Therefore, the question arises, "How much can the caustic be reduced?" The answer is that it varies somewhat according to dyestuff and depth of shade, and must be determined by experiment. I have some data here which I have arranged in tabulated form, showing that the quantity of caustic soda usually recommended can be reduced without any great loss in strength. These figures are based on laboratory tests on cotton:

Caustic Soda

	Usual Amount		Decreased Amount	
Color—10% dyeing	%	Conc. gms-liter	%	Conc. gms-liter
Blue GCD	12	6	4	2
Yellow G	12	6	4	2
Jade Green	12	6	7	3.5
Pink FF	12	6	5	2.5
Violet RR	12	6	4	2
Golden Orange G...	12	6	5	2.5

It was now thought that there was a possibility of using this information in the application of vat colors to pure silk. This fiber has been successfully dyed in the skein for some little time. A partial neutralization of the caustic soda by sodium bicarbonate is a method which has been recommended. This, however, does not reduce the alkalinity in terms of Na_2O. A number of so-called "protective colloids," of which animal glue is probably the most common, have been used. Aids to penetration, such as Neomerpin H, Pyridine, etc., are employed. Is it possible, therefore, by using a combination of reduced alkalinity, and other means, to obtain more satisfactory dyeings on pure silk? That is the thought I want to leave with you as deserving of consideration for future development in application of vat colors.

Generally speaking, the indigoids or thianthrenes are best adapted for this work, due to their greater affinity as a class than the anthraquinones. There are, however, many of the latter which are very well suited. It is my good fortune to have for your inspection dyeings on pure silk piece goods made in a semi-practical jig of several vat colors.

These are tabulated as follows:

Caustic Soda

Color	% Dyeing	Ozs. per 100 Gals.	Grams per Liter
Anthrene Jade Green Supra..	12	43	3.2
Thianthrene Brilliant Red 3B.	10	27	2
Anthrene Golden Orange G..	12	27	2
Thianthrene Orange R.....	10	27	2
Thianthrene Scarlet GP	10	34	2.5
Anthrene Violet 2R.....	3	27	2
Thianthrene Pink FF	1.5	47	3.5

Hydrosulphite

Color	% Dyeing	Ozs. per 100 Gals.	Grams per Liter
Anthrene Jade Green Supra..	12	35	2.6
Thianthrene Brilliant Red 3B.	10	24	1.8
Anthrene Golden Orange G..	12	26	2
Thianthrene Orange R.....	10	24	1.8
Thianthrene Scarlet GP	10	24	1.8
Anthrene Violet 2R	3	22	1.6
Thianthrene Pink FF	1.5	30	2.2

Constants, bath ratio, 1:25; glue, 3 per cent on material; Pyridine one-half pint per 100 gallons.

There has been no appreciable tendering of the silk; the dyeings are level; the penetration is quite good. The general fastness, of course, is about the same as that obtained with the same colors on cotton and viscose.

As I said earlier, if soluble vat colors are the only ones which will solve the application of faster colors to silk, American manufacturers will supply them. Surely, however, we want to investigate to the fullest the latent possibilities in what has already been supplied.

Vat colors of American manufacture offer a complete line of shades; they are available; they are equal to any that are being imported; they have excellent tinctorial value and stand as a monument to American scientific genius.

If I can close this paper feeling that I have indicated further possibilities of their application, I shall feel that the time spent in its preparation has been profitable.

Chairman Killheffer—The program called for a five-minute recess during the afternoon, but we fell very much behind in our program in getting started so with your permission, instead of the five-minute recess, I am going to call on Mr. Cady, the Chairman of the Committee on Prize Awards, to make his report which will only take a few minutes.

W. H. Cady—Mr. Chairman and Gentlemen: This Committee was appointed by the Council to award the Association prizes for the best papers read at meetings and published in the AMERICAN DYESTUFF REPORTER during the year beginning December 1, 1925, and ending November 1, 1926. The Committee with the approval of the Council has voted the following awards:

Seventy-five dollars to Dr. E. K. Strachan of Brown University, for his paper, "The Accurate Measurement of Hydrogen Ion Concentration as an Aid to the Textile Chemist," presented at a meeting of the Providence Section;

Fifty dollars to William D. Appel, for his paper, "A New Lamp for Fading Tests," presented at the last Annual Meeting;

Twenty-five dollars to Walter E. Hadley for his paper, "A Brief Resumé of the Disposal of Trade Wastes," read at a meeting of the New York Section. (Applause.)

Chairman Killheffer—We will now have a paper on "The Chemical Constitution and Fastness Properties of Colors," a very interesting subject, I am sure, by Dr Wuth.

. . . Dr. Berthold Wuth presented his prepared paper, passing out samples in the way of illustration:

The Chemical Constitution and Fastness Properties of Colors

By DR. B. WUTH
Ciba Company, Inc.

Fastness of dyes and colors is an old and much debated problem and its solution is more assiduously sought to-day than ever. Up to the days of the aniline dyes there existed two distinct classes of dyers, the fast color dyers and the loose color dyers—in French known as *les teinturiers au grand teint et au petit teint*—so named after the two volumes of the excellent work of the French Minister Colbert: *"Instruction generale pour la teinture des laines de toutes nuances et pour la culture des drogues et des ingredients qu'on y employe."* The fast color dyers were restricted for the production of their colors to the use of woad, indigo, sumach, gallnuts, madder, wau, cochenille, kermes, terra marita, curcuma, etc., whereas loose shades were produced with safran, brazil-bark, campeche, fisct, litmus, orleans, orseille, japan-bark, etc.

Under such circumstances the problem of fastness was simple, but the introduction of the fugitive aniline dyes rendered the line between fast and loose colors to a great extent indistinguishable. The scientific achievements in color chemistry did actually not improve but rather deteriorate the fastness of color, and it was many years after the discovery of the first aniline dye that resistible colors could be produced on animal and vegetable fibers with chemical synthetical products.

Influence of Constitution on Shade

The range of azo dyes and of the derivatives of triarylmethene, etc., seemed inexhaustible and therefore also the possibility of producing any desired shade in any desired degree of fastness. Accordingly scientists sought at an early date to find constant connections or relations between chemical constitution on the one hand and color and fastness on the other hand in order to be able to solve given problems on a theoretic basis and to eliminate endless empiric experiments. Thus in the course of time there originated the still very incomplete theory of the influence of the constitution of dyes on the shade and fastness of color.

It is a simple matter to define exactly the shade of a primary color as each primary color has its distinct position in the solar spectrum. With secondary colors it is much more difficult, and tertiary colors with the intermixtures of white, black and gray are almost indefinable. How extremely difficult a classification of colors is, becomes apparent on perusal of the marvelous work that has been done in this direction of which that of Oswald is especially elaborate and prominent. None, however, is practically perfect, a fact proved by the limited success in introducing them for technical purposes. If colors themselves cannot be strictly classified, how much more difficult must it be for the scientist to build up the chemical molecules *ad libitum* for the production of a certain color. The actual work accomplished in this direction is certainly great, but it is still fractional even in its limitation of deliberating constitutionally the direction of color in the spectrum.

An example of the methodical influence of chemical constitution on the change of color is found in the alkylation and halogenation of magenta or parafuchsin. Methylation of parafuchsin leads to Methyl Violet 2B and Violet Crystals, methylation and genxylation to Methyl Violet 6B, through the further modifications to Malachite Green and Brilliant Green and to the halogenated Turquoise Blue.

Influence of Impurities

The influence of impurities and of by-products in the manufacture of a dye on the purity of the color can also be typically observed in magenta which according to the amount of these impurities and by-products yields dyes such as Cerise, Grenadine, Marron, Cardinal and finally Phosphine.

Technically of greater value was the observation of systematic relations between constitution and color in the group of azo-colors, both direct cotton dyes and acid dyes. Numerous other examples could be mentioned, but it would require more than the allotted time to enumerate them.

From an early period of dyestuff chemistry we have such proofs of the perception of certain connections between constitution and color; much later a similar connection was observed between constitution and fastness. Few specific publications on this question are to be found in literature, nevertheless it may be said that this study has produced more of a positive nature for the industrial use of dyes than has the parallel study pertaining to color.

Some early examples of which brief mention may be made were surely haphazard observations. As an illustration in the basic group let us take the influence of an ethyl group in the carboxyl rest in Rhodamine. We reach here a certain point of contact between the influence of constitution on color and on fastness. From the faster diethylrhodamine we obtain the considerably more fugitive, but the brighter, the more beautiful, and more yellowish Rhodamine 6G. In this case the constitution is changed in order to influence the color without considering the change in fastness; on the other hand, however, the faster diethylrhodamine can be produced from Rhodamine 6G by elimination of the ethyl group from the carboxyl rest.

A typical example in the class of direct cotton colors is the increase in fastness obtained by the alkylation of Brilliant Yellow to the valuable Chrysophenine. Further, the influence of the sulphogroup on triarylmethene dyes is perhaps worth mention, whereby the basic character is destroyed and the valuable group of acid dyes is produced which as regards affinity for the fiber and fastness to alkali show considerable advantage over the mother dyes.

From these empiric beginnings up to the scientific and methodic modulation of the indigo molecule which has given us the interesting, important, valuable and complete range of color of the indigoid vat dyes was a long way of earnest research and keen observation. The speaker has taken upon himself to draw a short sketch of constitutional changes in fastness from the start up to the present time in which water-soluble complex metal compounds of technically valueless dyes represent substantive dyes of remarkable fastness.

Increasing Fastness by Constitutional Change

The most generally known methods to increase the fastness of a dye are all based on a constitutional alteration of the molecule, but the methods in practical use necessitate two distinct steps. The dye chemist builds the dye molecule so as to react in a certain manner, but the final change of the constitution is left to the dyer or printer as the case may be.

Such is the case in the large group of diazotizable,

direct dyeing cotton dyes. They are all azo dyes of various structure, but all possess the common character of containing one or more reactive amido groups. That these be present is the problem of the dye chemist who has in view the subsequent change in constitution to be effected by the dyer. It is the colorist's task to find the suitable conditions under which the soluble amido-body is converted into the soluble diazocompound, and it is finally the dyer who couples this compound with a phenol to a new molecule giving the same shade or a different shade than the original dyestuff and possessing greater resistance to external influences. A typical example of an amido dye which changes both shade and fastness with the change of the molecule is the well known Primuline. Many change shade hardly perceptibly; others more but seldom beyond one step in the solar spectrum.

The last step in this process, the combining of the diazotized amine with the phenol is erroneously spoken of as a development. It is not a development; it is a coupling and the reaction is from a chemical standpoint, identical with the process of producing fast colors by coupling direct dyes on the fiber with diazotized amines, such as p-nitraniline. In these cases the dye is a phenol and to this the diazotized amine is added. The number of the latter dyes is smaller than that of the former and the process is more complicated and somewhat tricky, requiring skill as the diazotation of the nitraniline in substance is left to the dyer who in most cases is unaccustomed to such chemical work.

These processes are lengthy and not as simple as a direct dyeing; they are therefore only adopted where a degree of fastness is required unobtainable with a direct dye without chemical change of its constitution. The dye on the fiber is constitutionally different from the original dye, and it is the change of constitution that is responsible for the change in the fastness properties. Salt in direct dyeing does not influence the constitution, it acts merely mechanically; hence the lack of influence on the fastness of color.

Relation of Mordant to Fastness

The production of insoluble azo dyestuffs on the fiber with non-dyeing amines is an entirely different matter, as no dyestuff is present on which a constitutional change could take place. This process was the foundation of the mechanical theory of dyeing, and it may well be a mechanical process as far as naphthol is used as a phenol, but with the introduction of oxynaphthoic acid and its derivatives the mechanical theory must give way to the colloidal theory of absorption on account of the distinct affinity between fiber and phenol. We shall revert later to the developments in this line.

Again we see chemists and dyers working hand in hand in the production and application of the numerous mordant colors, the chemist bestowing the dye with its constitutional affinity for a mordant, the dyer making a correct choice of the suitable mordant and applying it correctly. On the correct choice of the mordant depends the fastness of the resulting color. In a broad sense this includes the alizarines, the direct cotton dyes and especially acid dyes which can be aftertreated with metal salts. Here again we have a two-stage constitutional upbuilding of a fast dye on the fiber from a fugitive dye.

The alizarines as such are not fast dyes; on the contrary they are practically worthless for dyeing without being transformed into their metal lake. This transformation produces the fastness, but the formation of the lake is not only due to the production of the metal lake; it is also dependent on the structure of the alizarine itself inasmuch as only such oxy-anthraquinones possess the quality of a dye which contain the hydroxyl group in ortho-position. Therefore, it is clear that the production of a fast color with alizarines is dependent on the chemical constitution.

With few exceptions it is not possible to produce a fast color with a water-soluble substantive dye, and the majority of fast colors on wool are produced by a combination of a water-soluble substantive dye with metal. Here again the chemical constitution of the substantive dye determines the adaptability for the metal treatment. The variety of the active groups and their positions which enable the formation of metal lakes is too large to enumerate here, but it may be said that the carboxyl group and the hydroxyl group in ortho-position are by far the most important.

The increase of fastness of direct cotton dyes by combination with aldehydes on the fiber also falls into this chapter, but the number of such dyes is so small as to render further discussion unnecessary.

So far we have only spoken of water-soluble dyes, but in modern dyeing the insoluble dyes, the sulphur and vat dyes, are of eminent and increasing importance. Here the fastness is primarily not due to a constitutional modification, but is based on the insolubility itself. Fastness, however, can only be obtained where the insoluble dye is brought into contact with the fiber in soluble form. In a paper I read before a section of this Association some time ago, I put forth that the correct degree of solubility determines the fastness of a dyeing with insoluble dyes; that means to say, that as these dyes in their soluble form as salts of their leuco compounds are typical colloids, the highest degree of fastness can only be attained at a fixed and specific degree of dispersion. To obtain and maintain this degree of dispersion is the task of the dyer who can produce varying degrees of fastness by correct or faulty manipulation. Highly dispersed, the dye will combine intimately with the fiber; otherwise a large proportion will be deposited mechanically upon the fiber, and

is readily removed by mechanical means, such as rubbing and washing; i. e., the color is not fast.

Here we have a case that a constitutionally fast dye can be spoiled by the dyer, but the technical value of such insoluble dyes is based on their constitutional structure. They must possess the property of being readily con verted into their proper dyeing state of colloidal solution by simple technical means. That this is not always the case is shown by a vat dye of unrivaled beauty and fastness, but constitutionally not applicable to the textile fiber. A short explanation may interest some of the members present. The action of benzoylchloride on Indigo leads to Indigo Yellow 3G and Ciba Yellow G, two valuable dyes, but in replacing the benzoylchloride with phenylacetic-acid-chloride the original N-azyl derivative forms in secondary reaction a condensation product of a novel type which cannot be used as dye.

Viewed from the right standpoint, dye chemist and dyer work together on the construction of the sulphur or vat dye molecule on the fiber, inasmuch as the chemist builds the insoluble dye in a manner to permit the dyer to apply it to the fiber by the means at his disposal, and the dyer treats and changes the dyestuff molecule, in order to obtain a fast color.

Fastness Is Chemically Constitutional

At this point we arrive at the most marked and most interesting development in color and textile chemistry as far as the contention goes that the degree of fastness of color is dependent on and can be influenced by the chemical constitution of the dye. Indigo on cotton possesses but mediocre fastness. Bromination leads to much superior products which find their climax in the tetrabrom stage. Brominated naphthalin indigo are the fast Indigoid Greens, methylation of Indigo improves the fastness to chlorine, the valueless Indigo Red gives fast heliotrope and violet, halogenation of Thio-indigo Red leads to the faster reds and Bordeaux and other modifications to orange, gray, etc.

It would seem apparent that the fastness of a dye or a color in the textile industry is chemically constitutional and can never be obtained by mechanical means as in the manufacture of pigments. I remind you of the fugitive Malachite Green and its fast precipitate on green earth. Everywhere joining the creative hand of the dyestuff chemist we observe the chemically intentional change of constitution by the dyer leading to the completion of the molecule and to the attainment of fastness, just as without the hand of the master even with the most beautiful colors no picture is produced on the canvas.

If we turn our thoughts back a decade or so, we find that with very few exceptions all substantive dyes are fugitive, and for fastness a constitutional change was imperative. Textbooks on dyeing generally speak of substantive and adjective dyes, the substantive being those which dye without any auxiliary agent, the adjective requiring some agent or mordant for their fixation on the fiber. We take as substantive the basic and the acid triarylmethene dyes on animal fiber, the azo dyes (cotton and acid dyes) on vegetable and animal fiber, and in a wider sense also sulphur and vat colors; as adjective the basic dyes on vegetable fibers and the so-called true mordant dyes of both sexes.

Substantivating Adjective Dyes

Now, if one would circumscribe the meaning of the term adjective somewhat wider in the ethymological sense of the original Latin word *adjectio*, the addition of something, then all such dyes could be classified as adjective which for their application require the *adjectio*—the addition of some chemical reagent for their fixation. In this case all sulphur and vat dyes and also the azo dyes coupled and aftertreated with metal salts would come under the adjective heading and the thesis would be permissible that all substantive dyeings are fugitive and adjective dyes must be employed for fast colors. No rule without exception: consider Chrysophenine, Kiton Fast Yellow and Red, Alizarine Saphirole, etc.

I intentionally took the viewpoint of the last decade, as we are working in an era of enormous evolution with the object of converting chemically adjective dyes, as taken in the wider sense, into substantive dyes, naturally with the same fastness properties. Fastness is the increasing demand of the day, but at the same time production is the leading economic feature. The ideal situation would be to produce fast shades with substantive dyes, and this fact has outlined the work in the research laboratories of the dye manufacturers for the last few years.

Neglecting chronological sequence I shall endeavor to summarize broadly the work that has been done in the last years to substantivate hitherto adjective dyes, whereby I may stray slightly from the caption of my paper in some cases.

To start with the basic dyes, typically adjective to cotton, some interesting work can be reported eliminating to an extent the use of a mordant and even the steaming in the case of printing. I refer to the reaction products of basic colors with volatile organic acids. After employing acetic acid it was found that formic acid gave better results, but this was discarded on account of the pungent odor of the vapors. It was replaced by the chlorinated acetic acids, mono-chloracetic acid, glycolic acid, etc., whereby deeper and faster colors were obtained. Later the ethyleneglycol or thio-di-glycol and still later lactic, malic, oxalic and phosphoric acid were found to be of good value.

I mentioned previously that the production of insoluble azo colors on the fiber was the mainstay of the mechanical theory of dyeing; how this, however, had changed with the introduction of the oxynaphthoic acid possessing affinity for the fiber; whereas a b-naphthol (Mol. W.) bath always remains constant in proportion of naphthol to the water after the passage of ever so much material, a bath containing the more highly dispersed b-oxynaphthoic acid exhausts rapidly and must be constantly fed to insure evenness of shade. This only by the way; for our subject of the substantivation of adjective dyes, the old Nitrosamin of the Badische Aniline und Soda Fabrik (Schraube & Schmid) forms the beginning in the azo series. To bring back this old and well-known discovery into our mind, we remember that in solutions of the majority of diazo compounds the action of free alkali accelerates the normal deterioration of these unstable substances by absorbing water and splitting off nitrogen. Under certain circumstances, however, the action of alkali leads to important technical results. The hydroxide of the diazo compound forms the nitrosamine of the original monamine through intermolecular change.

Nitrosamines in Insoluble Azo Dyes

These nitrosamines, which as such are not dyes and have been erroneously termed Iso-diazo compounds, are quite stable substances of an acid character. In form of their alkali salts they can be kept for considerable time, but on addition of a mineral acid to their solution the corresponding salt of the typical diazo compound is reformed. The nitrosamines of the primary amines are a a stable form of diazo compounds which have proved to be of great value.

Originally only one nitrosamine was used, the para-nitrophenylnitrosamine, but it was not substantive as for the color formation a coupling with a phenol, an *adjectio*, had to take place. Much later, after numerous stable diazo compounds had been made, insoluble azo dyes were put on the market as substantive dyes for cotton printing

These substantive azo dyes are mixtures of nitrosamines, stable diazo compounds with b-hydro-oxynaphthoic acid anilide. As an example may be mentioned the mixture of the nitrosamine obtained by the action of sodium hydroxide on diazotized m-nitro-p-toluidine with b-hydroxynaphthoic acid anilide; a red color of excellent fastness properties

A treatment with acid decomposes the nitrosamine and the free diazoamine couples with the phenol to the insoluble pigment. Contrary to the old Nitrosamine Red, this modern work furnishes us with practically a full range of shades which can be increased by mixture with substantivated vat dyes, to which we will now turn our attention.

The substantivation of vat dyes also dates far back. It gained but scant notice from a practical standpoint because a treatment either before or after application was necessary for complete development or fixation. I am referring to the production of Indigo on the fiber with o-nitrophenylpropiolic acid which is converted into Indigo with sodium xanthogenate in alkaline solution. The sodium bisulphite compound of o-nitro phenyllactic-acid-methylketon and the indoxylcarbonic acid should also be mentioned here. As already stated a complete substantivation had not taken place, but it was achieved in the dry sodium salts of leucoindigo in their various forms. The cost of these products and the fact that they did not eliminate the skillful vat dyer prevented the introduction in Occidental countries. We are given to understand that work in this direction is being continued and extended to the other vat dyes and we await the developments with interest.

Substantive vat dyes of other constitution, however, are in use to-day, and although they have not supplanted the insoluble vat dyes nor probably will in the near future, except for certain purposes, it is without doubt a very interesting development and a great step in the desired direction to shorten and simplify dyeing methods.

The first water-soluble Indigo derivative was made in 1740 by Barth by treating natural Indigo with sulphuric acid. This is the sulphonic acid of Indigo, still well known as Indigo Carmine. It is an acid wool dyestuff and has nothing in common with Indigo; therefore, it is not a substantive water-soluble vat dye. The soluble substantive vat dyes referred to are sulphuric acid esters of leuco compounds, probably the sodium salts of the enolic esters of leuco dyes and sulphuric acid, obtained, for example, by the action of chlorsulphonic acid on leuco bodies such as chlorobenzene, di-methylaniline, and pyridine in the presence of a tertiary base. They are neutral colorless salts, perfectly stable and readily soluble in water. The wording of the patent is: "Process for the production of fast dyeings on wool, based on the fact that the sulphuric acid ester salts of Indigo and other vat dyestuffs can be dyed in an acid bath like ordinary acid dyestuffs, and then by means of low temperature oxidation, the fast, insoluble vat dyestuffs can be reproduced on the fiber." A more substantive dye is hardly imaginable. Differing from Indigo it can be dyed on a percentage basis to any depth of shade.

Combining Soluble Vats with Other Colors

Being an acid dye the soluble vat dyes can be combined with other acid dyes. According to Peterhauser, after-chrome colors can be dyed along with the vat dye, the latter being developed in a fresh liquor. As the oxidation process is carried out at a low temperature, the after-

chrome color is only partially developed. The bath is therefore let off and refilled, the necessary small amounts of bichromate and acid are added and the development of the chrome color is completed at the boil.

Dr. Lloyd has pointed out the use for preparing standard dyeings of Indigo to use for the determination of the shade percentage of Indigo on dyed fabrics.

Of certain interest but in a lesser degree are these soluble vat dyes for calico printing, as the substantive character of a dye is not as important for the printer as for the dyer. As a printing color, however, one finds little advantage, if any, over the printing with the insoluble vat dyes. The preparation of the printing paste is no more simple, there is no less handling of the goods, and the process is not shorter. A new field, however, is opened for the printer by this discovery, inasmuch as they can be combined with the aforementioned phenol-nitrosamine mixtures. For example, a fast green can be produced with a printing paste containing the sodium salt of the sulphuric acid ester of a yellow vat dye, and the mixture of the nitrosamine of tetra-azotized dianisidine base with b-hydroxynaphthoic acid anilide.

The next work to be referred to is that on azo dyes to form the constitutional structure to render their substantive dyeings fast and to eliminate an aftertreatment for this purpose. So far science has only succeeded in eliminating the aftertreatment with metal salts, whereas we have to look to the future to bring us substantive dyes of the diazotized and coupled type.

Research Work on Metal Compounds

It is an old fact that certain blue cotton colors become faster to light when aftertreated with copper salts. Such dyeings are not satisfactory, as the increase in fastness decreases by washing. This fact would lead to the supposition that the copper is not constitutionally bound to the dyestuff molecule. Copper compounds of the same dyestuffs made in substance are insoluble and cannot be used as dyes. This investigation, which was carried out approximately at the same time as Werner's work on soluble complex metal compounds, led to the interesting and valuable discovery that azo dyes of certain constitutions form soluble copper compounds which possess great substantive affinity for the cotton fiber. As was anticipated, these soluble copper compounds possess an extreme fastness to light which is lasting, that is to say, which does not decrease by frequent washing. Furthermore, they were not restricted to blue as was the case with the aftertreatment, but a full series of fast colors could be produced.

By this discovery the adjective dyeing of cotton dyes with an aftertreatment with copper was superseded, improved and widened to an extent that it is now possible to dye cotton substantively in all shades fast to light. Certainly a great step in the right direction. It followed logically that the research would be extended to other metal compounds and especially to chromium, as this metal had proved to have such valuable effects in the aftertreatment of azo dyes. The cotton dyes did not react in the desired direction, but it was unexpectedly found that complex soluble chrome derivatives of the oxyanthraquinonesulphonic acids are formed by treating the oxyanthraquinonesulphonic acids or their salts with chromoxide salts at the boil. This discovery was followed by the observation that also azo dyes containing chromable sulpho and oxy groups which are derived from diazotized o-aminophenols, o-aminonaphthols or diazotized anthranilic acid or from derivatives of these bodies or which contain rests of salicylic acid or its derivatives, form soluble chromium complex compounds. The solubility of these dyes is so high that they cannot even be salted out of their aqueous solutions by the addition of indifferent salts. Correspondingly they have no affinity for the wool fiber, and have only been used in cotton printing and the manufacture of inks.

It was further found that ortho-oxyazo dyestuffs sensitive to copper can be transformed into well defined copper compounds soluble in water, from which the copper cannot be precipitated with sodium carbonate, soda lye, and ammonia; also that o-oxydiazo dyestuffs derived from the polycyclic ring systems containing a CH_2 group able to combine with a diazo group, e. g., di-ketonhydroindon, perinaphthindandion, 3-oxy-1-thionaphthene, ketocumacan or o-oxy azo dyestuffs derived from ortho-carboxylated benzoicacetic acid* form soluble dyes which dye wool evenly and extremely fast to light and fast to washing substantively from an ordinary acid bath. Another method of manufacture was to combine two azo dyestuff components, one of which is an o-oxydiazo compound of the aromatic series in the presence of a copper compound.

These soluble copper compounds, though extremely fast to light and very fast to washing, did certainly widen the range of colors obtainable by an aftertreatment of acid dyes with copper sulphate but did not excel the latter in their degree of fastness and did therefore merely increase the number of fast-to-light acid dyes but in no way supplanted the so-called afterchroming method used in fast wool dyeing.

Water soluble substantive acid dyeing dyes fast, as the afterchrome dyes were found in the chromium compounds of azo dyes, especially o-oxyazo dyes and also chromium compounds of gallocyanine dyestuffs giving fast colors without mordants in calico, wool and silk

*Or of o-oxyazo dyestuffs derived from a betacetonaldehyde derivative in which an alkyl-alklyoxy or alphylamido group is substituted for the aldehydic hydrogen.

printing. A process of manufacture of such a chromium compound may be of interest. An o-aminophenol compound is treated with a chromium compound in a hot aqueous medium; the thus obtained chromium compound of the o-aminophenol is diazotized and the resulting chromium compound of the o-oxydiazo body is combined with an azo dyestuff component containing at least one group able to be chromated, and the thus obtained half-chromated o-oxyazo dyestuff is finally treated in a hot aqueous medium with a chromium compound.

The properties of these new substantive wool colors were given briefly and precisely by Gilbert T. Morgan, F. R. S., in an address on recent researches on mordant dyes before the Worshipful Company of Dyers at Dyers Hall, London, and I may be allowed to quote him:

"A process has recently come into vogue which consists of converting the dye, usually a dihydroxyazo dye, into its chromic lake. Provided that the lake is sufficiently soluble it can be employed as a dye. These soluble lakes can be applied in metallic dye baths because, unlike the original dyes, they are no longer sensitive to metals and metallic oxides, as when once the stable cyclic systems have been established by interaction of the metallic hydroxides and the chelate groups of the dye there is very little tendency for the displacement of the implicated metal by some other metal.

"The shades are fast to light and milling. They are applied from a sulphuric acid bath like ordinary substantive acid colors, but they possess the fastness associated with chrome or mordant dyes."

Science, gentlemen, is coming day by day nearer to the point where it can fulfill the desires of industry. The chemical constitution of dyestuffs is the source from which the general demand for fast colors at a popular price must flow; there is, for the production of fast shades at marketable prices, no other man to go to than the man who builds the molecules. The work of the scientist in producing such products which increase and cheapen production, by his researches does not, as it might seem, reduce the necessary skillfulness of the dyer. On the contrary, the application of the somewhat complicated substantivated dyes calls for a higher standard of the applicator, the dyer and printer. He must be a learned mason in the upbuilding of his colors with these new dyes, more so than his predecessor, who simply followed the recipes in his father's notebook. To-day the dyer's work is similar to the golden rule of the mechanic's: the shorter the time of dyeing, the more experienced observation on the part of the dyer is needed.

Efficiently hand in hand the chemist and the colorist can complete the evolution we are now going through of widening our knowledge of the relationship between the chemical constitution and the fastness properties of color. (Applause.)

Chairman Killheffer—We have one more paper on the program that I was supposed to present. The hour is well advanced and the paper is not too short. I will do what I can to get through it and give you the fundamentals of it. I will skip a bit here and there so that if possible it won't become tiresome.

. . . Dr. Killheffer presented his prepared paper in skeleton form, owing to the lateness of the evening; it is published in full below, however:

Solvents Made by the Hydrogenation Process, Their Manufacture and Some of Their Uses and Applications in the Textile Industry

By Dr. Elvin H. Killheffer
Vice-President, Newport Chemical Works, Inc.

The hydrogenation of various products has been practised for quite a considerable time, perhaps some of the best known instances being the hydrogenation of various oils. Quite a little experimenting was also done in the way of the hydrogenation of various hydrocarbons, but it really needed the artificial impetus created by the war to hurry the work and bring the products to a point where some of them at least could be put to practical use. Such certainly was the case with Tetralin, which is tetra-hydro-naphthalene. Naphthalene, as you know, is a white, flaky compound, whereas the tetra-hydro-naphthalene is a water-white liquid. During the war such products as turpentine and motor fuel became very scarce indeed in Germany, and it was natural, therefore, that a new solvent like this one should be tried out for a number of uses. As a matter of fact, one of its first uses was that of a turpentine substitute in paints, and because of its great powers of solubility it could very readily be used in place of solvents, which had become quite scarce and very expensive.

In the search for substitutes for motor fuels there was finally developed a fuel composed of benzol, alcohol and tetralin used in approximately equal amounts, and this fuel was used to quite a considerable extent.

As the more urgent demand for such substitutes passed, there were left producing units for compounds which had really not been carefully and systematically studied up to that point as to their many possible uses. The result is that only comparatively recently have such systematic studies been undertaken. The indications are that many most interesting and diversified uses will be found in addition to the already large number of uses indicated by the work so far accomplished.

The manufacture of these hydrogenated solvents was taken up in the United States by our company, beginning with the hydrogenation of naphthalene and the consequent production of tetralin. This was later followed by the hydrogenation of phenol to produce Hexalin, which is

hexa-hydro-phenol, or Cyclohexanol. Next produced was Iso-propanol, which is isopropyl alcohol, in practically pure form by the hydrogenation of acetone, this method and product differing quite materially from the product obtained by the cracking of petroleum oils. Next came the hydrogenation of cresol to produce Methyl Hexalin and later the hydrogenation of pine oil to produce Hydroterpine.

While we have produced some other products in a small way, i. e., tetra-hydro-naphthol, etc., the ones already enumerated represent the present-day commercial productions, and it will be to these named solvents that we will give a little further consideration.

Briefly, the process of hydrogenation as we practice it consists in the addition of gaseous hydrogen to the product to be hydrogenated in an autoclave under the correct conditions of temperature and pressure, and in the presence of suitable catalysts. The question of time, temperature and pressure varies quite considerably between products. With some the hydrogenation proceeds smoothly and quickly, and in the case of others the absorption of the hydrogen is much slower and at higher temperature and pressures. As an instance of this is the difference in the production of Tetralin (tetra-hydro-naphthalene) and Decalin (deca-hydro-naphthalene). The reaction proceeds quite regularly up to the point where the Tetralin is formed, but the further hydrogenation to Decalin proceeds slowly, and at both higher temperature and pressure.

In the hydrogenation of these various hydrocarbons a very high degree of purity is necessary in the various materials used, otherwise the catalysts are quickly poisoned and no absorption of hydrogen takes place. For instance, in the case of naphthalene the ordinary purified naphthalene is not suitable, but it must first undergo a special process of purification before it can be successfully hydrogenated by this direct process in the presence of a catalyst.

Tetralin

Tetralin is made by the hydrogenation of naphthalene. It is a water-white liquid with a boiling point of 206 deg. Cent. (402.8 deg. Fahr.) and a specific gravity of 0.975, flash point 80 deg. Cent., freezing point minus 25 deg. Cent.

There are two known tetra-hydro-naphthalenes, one is formed by the action of phosphorus and hydriodic acid on naphthalene. This gives the 1:4:5:8, or a-tetra-hydro-naphthalene. The product produced by the direct hydrogenation of naphthalene in the presence of a catalyst is the b-tetra-hydro-naphthalene, and this is the product referred to in the subsequent discussion.

Tetralin is a very stable chemical compound even at its boiling point. It can be sulphonated or nitrated. The sodium sulphonate has a number of interesting possibilities which are now being made the subject of a rather thorough investigation. Tetralin does not mix directly with water, but will readily combine with solutions of soap or soluble oil. Such solutions are, however, not perfect, and a separation takes place after standing for some length of time. A slight agitation causes the substances to again combine very readily, but it is not what would be called a stable solution and, before a really stable solution of this sort can be prepared, there must be some addition of Hexalin or Methyl Hexalin which acts as a homogenizing agent as will be pointed out later.

It is non-poisonous, non-explosive and non-inflammable. Experiments conducted in Europe show that even with an internal dosage of Tetralin only slightly toxic properties are observed.

Of some interest is a comparison of boiling points of Tetralin as compared with some other well-known solvents.

Comparative Boiling Points Expressed in Deg. Cent.

Acetone	56
Alcohol Absolute	78
Alcohol Methyl	60
Toluol	111
Spirits of Turpentine	160
Benzene	80.4
Carbon-Tetra-Chloride	76.74
Pyridine	114.5
Tetralin	206

Tetralin is a very powerful solvent for organic substances, and it is an excellent solvent for all kinds of fats, oils, waxes, resins and soft gums, but does not dissolve shellac or the phenol-formaldehyde resins.

There is a very great deal of work to be done in the determination of the relative solubilities of various substances in Tetralin as compared with other organic solvents. This work is being carried on now. The following table indicates the comparative solubility of ordinary beeswax in a few different solvents:

Tests at Room Temperature (22.5 deg. Cent., or 72.5 deg. Fahr.)

Solvent, 100 c.c.	Amount Beeswax Dissolved grams	Remarks
Linseed Oil	0.60	Clear
Carbon-Tetra-Chloride	4.88	Clear
Hydroterpine	2.92	Slightly cloudy
Tetralin	6.80	Clear
Hexalin	0.80	Clear
Isopropyl Alcohol	0.72	Milky
Ethyl Alcohol C.P.	0.40	Cloudy
Benzol, 90 per cent.	7.04	Clear
Methyl Hexalin	0.52	Cloudy
Turpentine	1.48	Clear

These differences in solubilities continue in approximately the same ratio as the temperature is increased, except that, of course, in the case of beeswax, when you make much stronger solutions, you either have a paste or solid as soon as your temperature diminishes.

Tetralin has already found a multiplicity of uses, its principal one at the present time probably being in variout detergents and liquid soaps. Its value in such compounds is its high solvent power over a wide range of oils, gums and waxes. Its high boiling point is, of course, very valuable in this connection, as it can be used in various detergents, even though they are used at high temperature, and where Tetralin is employed as the organic solvent, there is no danger of its loss by evaporation at these higher temperatures. For many textile soaps and detergents it is brought into a form soluble in water by the addition of Hexalin and a little soluble oil or soap.

The resulting combinations have the further valuable property of reducing the surface tension of liquids which in conjunction with the high solvent value makes the compounds of great value for wetting out materials, causing quickly their complete penetration, etc.

At this point it might be well to digress for a moment from a strict discussion of the solvents themselves, and consider a little further the properties of some of the special detergents, wetting out compounds, aids to penetration, etc., which have as their base these hydrogenated products; in other words, what it is about them that makes them valuable for these various purposes. Stated briefly it is a combination of:

a. Their powers of solubility.
b. Their property of lowering surface tension.
c. Their property of forming emulsions with all kinds of substances.

As is well known, cotton, as an example, is quite resistent to thorough wetting due to its content of wax and oily substances, air, etc. Then there is in addition the surface tension of the liquid or liquids in which the cotton is to be wetted. As a factor in favor of the ready wetting out of the cotton is the force of capillary attraction, and when the wetting agent is of such a character that it readily lowers the surface tension of the liquid, dissolves and emulsifies fats, waxes, oils, etc., that may be present, then the full force of capillary attraction also comes into play and we have the best form of wetting or penetrating agent. In this connection several articles have recently appeared in Melliand's Textilberichte on the subject of wetting out agents, and in both of these articles direct comparisons are made between a number of rather well-known products, and tables are given showing the results obtained. One of the articles referred to is that by Dr. J. Auerbach in the August, 1926, issue, and the other an article by Dr. W. Seck and Dr. H. Lachman in the October, 1926, issue. As to the net result of the work described in both of these papers, they report that Neomerpin N, Neomerpin and Nekal are by far the best, all of which are made from hydrogenated products.

Some of the special uses to which Tetralin has been put I will simply outline briefly. Due to its high flash point, it can be used with much greater safety as a dissolving and thinning agent in various lacquers, varnishes and paints than the commonly used naphtha, toluol and benzol. It finds quite a use in the manufacture of various substances, like shoe creams, because the cream does not dry up nearly as readily as with other solvents like turpentine. Some use has been made of Tetralin in internal combustion engines in combination with alcohol and benzol.

The specific heat of Tetralin is 9,720 calories, and its high specific weight accounts for the greater power per gallon than gasoline and benzol. A tank holding 26.4 gallons will contain about 160 pounds of gasoline with 798,000 calories, or 189 pounds of benzol with 834,000 calories, or 215 pounds of Tetralin with about 950,000 calories.

The flash point of Tetralin is 79 deg. Cent., which is particularly desirable in the use for airplanes. Tetralin has certain lubricating qualities and will not corrode metal. Samples of iron, steel, aluminum, copper bronze and brass were exposed to Tetralin for years, but no trace of corrosion were noticeable.

Tests.—Pure Tetralin was tested in high compression motors, and it was shown that even the highest compression did not give pre-ignition.

The problem being to find a motor fuel which could be used with advantage in the low compression motor of to-day, which would stop the knocking of the engine, mixtures of Tetralin with other fuels were tested. This was done on a scientific basis at the testing station for explosion motors of the Technical University of Berlin.

Mixtures of one part of Tetralin and one part of gasoline (.720 and .735 specific gravity) gave the best results, also mixtures of Tetralin with benzol and mixtures of Tetralin, benzol and alcohol were found practical. The limits established were that 10 per cent of the total mixture should distill below 100 deg. Cent., and that 30 per cent should distill below 150 deg. Cent. The specific gravity of such mixtures should correspond approximately to the gravity of benzol to avoid special adjustment of the carburetors.

After the scientific tests had been completed and considerable theoretical data accumulated, practical tests of such mixtures were made on the road. A mixture of 50 per cent benzol with 25 per cent Tetralin and 25 per cent alcohol was used. The motor was started as easily as

with gasoline; there was no tendency for pre-ignition, and no knocking was noticed even under severe testing conditions. The combustion was absolutely complete according to gas analysis made of the exhaust, and no carbon deposit was noticed on spark plugs even after great distances had been covered. The spark plugs were examined and found remarkably clean. Spark plugs which had been used in gasoline engines and which showed large deposits of carbon and no longer gave good results with gasoline, were attached to the cylinders. It was observed that in a short time the fuel containing Tetralin had removed the carbon from the spark plugs to such an extent that they were absolutely clean. Also no accumulation of carbon in the valves or other parts of the motor occurred.

The only changes made to adapt the motor to the new fuel was to supply additional warm air to pre-heat the fuel mixture. The carburetors were adjusted to heavy benzol, which is essential.

Quite a little work has been done along the line of removing printer's ink from newspaper by a process of flotation in which Tetralin-Hexalin combinations are the fundamental reagents.

Tetralin, because of its high boiling point, its stability and its high dissolving powers, has been found of a good deal of value as a crystallizing medium for various substances. Further information along this line will be forthcoming later, as will be also further information as regards its powers of solubility for various substances.

A use of Tetralin that is of growing importance is as an absorbent for casing-head gas. It absorbs from 5 to 10 per cent as against 1 to 2 per cent for straw oil, which is the absorbent generally used. The United States Bureau of Mines reports on the recovery of gasoline in the United States by the absorption processes as being 70 per cent, whereas by the Bregeat process the absorption is 95 per cent. Tetralin is so active as an absorbent that even the tail gases that have already been put through the straw oil absorption process can be brought up to the 95 per cent yield figure by a further passage through the Tetralin system. The gasoline so resulting has a very high purity. Tetralin does not absorb the sulphur content. In this case also, the high boiling point of Tetralin is very valuable from the angle of recovery. In a plant for treating several million cubic feet of gas per day, the absorption system contains 30,000 gallons Tetralin and the daily loss is only about 40 gallons. In an absorption plant of the same capacity approximately four times the amount of straw oil must be used and even then, as pointed out, with a lower recovery.

Decalin

In the hydrogenation of naphthalene into tetra-hydro-naphthalene four atoms of hydrogen are introduced, as the name implies, whereas in deca-hydro-naphthalene there is a complete saturation with hydrogen, and the resulting compound is, therefore, not easily susceptible to chemical reactions. Decalin has a boiling point of 188 deg. Cent., a flash point of 57 deg. Cent. and a specific gravity of 0.895. Decalin, the same as Tetralin, evaporates without leaving any residue. It possesses a somewhat higher evaporating speed than Tetralin. It is a transparent liquid with a rather pleasant odor, and serves as a highly suitable thinner. Decalin has been sold abroad as refined Tetralin. It will not cause any decoloring, even in white lacquer.

On account of its high solvent power, it has been suggested and used in various forms of paint and varnish removers.

Decalin, like Tetralin, can be brought into watery solution by the use of a small addition of Hexalin soap

Hexalin

Hexalin is the abbreviated designation for cyclohexanol or hexa-hydro-phenol, and is produced by the hydrogenation of pure phenol. It is a neutral water-white liquid, and, like all higher alcohols, does not dissolve readily in water. It has a specific gravity of 0.945 (7.9 pounds to the gallon), and boils at 155 to 160 deg. Cent. Its flash point lies at about 68 deg. Cent. It will not decolorize on standing, and is very stable even at the boiling point and evaporates without leaving a residue. Like amyl alcohol, Hexalin has a high dissolving capacity for solid and liquid hydrocarbons, fats, oils, resins, waxes and the like.

Hexalin for Resins, Synthetic and Natural

The high dissolving power of Hexalin is of great importance; as, for instance, in connection with phenol formaldehyde condensation products. It has been found that Hexalin mixed with Decalin possesses an excellent solvent capacity for resins, and shows in particular the property of easily dissolving the condensation products of phenol and formaldehyde, which, as is well known, are not soluble at all, or not easily soluble in numerous solvents. In fact, a solution of these synthetic resins in a Hexalin-Decalin medium furnishes clear and durable solutions even when diluted with non-solvents. The solution obtained is suitable for lacquering wood and other substances, and does not dry any more slowly than turpentine lacquers, and leaves the resin in the form of a clear coating hard to remove from the foundation.

In connection with the dissolving of synthetic resins, other combinations of these solvents can be employed as, for instance, Hexalin can be substituted by one of its esters, namely Hexalin Acetate and the Decalin (deca-

hydro-naphthalene) can be substituted by Tetralin (tetra-hydro-naphthalene).

Hexalin has a high solvent power for gums and other products used in the varnish and lacquer industry, and in a subsequent paper soon to be published some tables of solubilities will be given.

In a number of German patents a great many diverse claims are made as to special uses and properties of Hexalin and a great deal of work is now being done toward confirming, if possible, the claims made, and as soon as this work is complete it will be published in an effort to reduce the present field of claims to the statement of exact facts. A few of these are the following:

Linoxyn Solutions

Linoxyn has been used to a great extent in the manufacturing of linoleum, but its application in the lacquer industry has been restricted because of the difficulty of finding a suitable solvent. It is true that Linoxyn becomes soluble in amyl alcohol and amyl acetate, but such solutions require months for their manufacture in order to remain clear and transparent. It has been found that clear, transparent and non-depositing solutions which can be further thinned with other lacquer solvents, can be obtained by the use of cyclohexanol or cyclohexanone. The solutions obtained dry to an originally sticky, but gradually tough and elastic film. The drying, of course, can be accelerated by the addition of siccatives. Linoxyn solutions are not only serviceable in the lacquer and varnish industry, but can be used in the manufacture of linoleum, artificial leather, etc.

Rubber Dissolving Agent

Cyclohexanol or its conversion products are capable of dissolving both crude and vulcanized rubber. Crude rubber can be wholly or partly dissolved with well-known volatile solvents, such as benzine, benzol, carbon-tetra chloride, etc., and vulcanized rubber with xylene, aniline, etc., in order to subsequently subject it to further treatment after removing the foreign ingredients and eliminating the solvents. In a number of the solvents the rubber swells up well, but is only partly dissolved. Large quantities of the solvent are consequently required which afterward have to be recovered. On the other hand, some of the solvents have the disadvantage that their solvent power is exerted only at relatively high temperatures.

It has been found that cyclohexanol and its esters, as well as cyclohexanone, exercise a solvent action both quickly and perfectly, and at lower temperature than is the case with most other solvents. Even where high temperature is worked with the high boiling point of cyclohexanol and the reduced fire risk afford great advantages. Tetra-hydro-naphthol acetate now appears much better for this purpose.

Combination of Celluloid and Rubber

It is well known that the difficulty of making a combination of celluloid and rubber is in the finding of a solvent in which both rubber and celluloid are simultaneously soluble. A number of the most common solvents of celluloid, such as acetone and amyl acetate, act as precipitating agents for rubber from its solution, while on the other hand celluloid is entirely insoluble in a number of the rubber solvents, such as carbon-tetra-chloride, carbon disulphide, etc.

It has been found that celluloid can be dissolved in Hexalin and that rubber can also be dissolved in Hexalin and the two solutions afterward combined. If this mixture is then applied to a glass plate, for instance, and the solvent allowed to evaporate, a fine celluloid-rubber film is obtained. It is, of course, possible to make some substitution of solvents as, for instance, Methyl Hexalin in place of Hexalin, and various proportions of celluloid and rubber can also be used, depending on the result that is desired.

Homogeneous Liquid Mixtures

Hexalin is valuable as a homogenizer when added to certain other solvents which by themselves are not miscible either with each other or with water. Also there are some solvents which are miscible with water in some proportions, but separate on great dilution. Other solvents will mix with each other, but are not clear. As an instance of this, mixtures of 50 parts of Tetralin (tetra-hydro-naphthalene) and 50 parts of spirit from milky solutions, whereas by the addition of 5 parts of Cyclohexanol these are converted into genuine solutions. Methyl Cyclohexanol and Cyclohexanone have the same properties in this respect.

In the case of Tetralin it is not directly miscible with water, but if the Tetralin is combined with some soluble oil, or soap, and a small percentage of Cyclohexanol added, the resulting mixture can be carried to practically any dilution with water without any separation of the solvents whatever.

A rather striking example of the effectiveness of Hexalin is in the case of tetra-hydro-naphthalene-sulphonic-acid-soda-salt, which is only soluble in water to a certain extent. If 35 parts of this salt and 65 parts of water are taken the soda salt will not dissolve in this amount of water. As is already known, Hexalin is not itself miscible in water, but if to the above 50 parts of Hexalin are added, the whole at once goes into a perfect solution,

and this solution is capable of dilution with large quantities of water without any separation of the components.

The homogenizing influence of Hexalin and its property of imparting new and novel properties to other compounds is a highly interesting one and, like quite a few other things mentioned, is now the subject of a great deal of study. Some of its properties in this respect will be referred to a little later in connection with lacquers.

Emulsifying Agents

The high dissolving capacity of Hexalin and Methyl Hexalin and their ability to form with watery soap solutions perfectly clear solutions which in turn possess high emulsifying properties has led to their use in the preparation of spinning oils, loom oils, etc., which are readily washed out with water.

It has been found that Cyclohexanol, which is itself insoluble in water, can be easily incorporated in an ordinary soap body, and that this dissolved in water results in entirely clear dilutions which, even under ordinary temperature conditions, possess a high dissolving and emulsifying property for neutral fats, waxes, fatty acids, solid and liquid hydrocarbons. These Cyclohexanol-soap mixtures can be used either solid, semi-solid or liquid wherever the removal of fatty substances is involved—as, for instance, in the textile or leather industries; and, besides, they afford excellent emulsifiers for all substances which cannot be easily, if at all, affected by watery soap solutions.

Hexalin and Methyl Hexalin in Soap

Hexalin has a not unpleasant odor, and one which is slightly suggestive of phenol, with also a slight suggestion of menthol. Methyl Hexalin perhaps has the odor suggestive of menthol developed a little more strongly than Hexalin. Hexalin is not changed by storing or slow evaporation; that is to say, it does not turn dark, as does phenol. It retains its water-white, oily character, and is in general appearance quite suggestive of gasoline. As far as the use in soap is concerned, the remarks made for Hexalin are equally effective as to Methyl Hexalin.

These are both used now quite extensively in the manufacture of soaps, liquid detergents and special emulsifying compounds. Their use in soap imparts very valuable properties, both as to solubility and emulsification value; and, of course, their high boiling point, as already referred to, prevents a loss of the solvent ingredients when the soap is used at high temperature.

The use of soaps prepared in this way is not confined to the textile industry, but finds a great value in the laundry and general household field because of the easy removal of dirt, fat, oil and even blood stains. In the presence of Hexalin, blood loses the capacity to coagulate.

Another point of great interest is that where Hexalin is incorporated in a soap other solvents, such as Tetralin, benzol, carbon-tetra-chloride and turpentine, can be incorporated also, if desired, and the resulting soap will produce homogeneous, water-soluble products which remain soluble in water, even in weak water solutions.

The peculiar odor of Hexalin is not disagreeable during the washing process and has no harmful effect on the workmen. It is also of importance to know that this odor does not adhere to the material, which after rinsing becomes absolutely odorless.

Hexalin in soaps will also dissolve such water-insoluble substances as magnesium and lime soaps. If hard water is used, the disagreeable feature of sticky precipitates of lime soaps is thus eliminated. Small additions of Hexalin do not affect the foaming of the soap. Larger additions, however, do act in the same way as equally large additions of other alcohols.

The presence of Hexalin in neutral soaps has the effect of retarding, up to a considerable degree of dilution, the hydrolysis of the soap.

In the manufacture of soap, Hexalin should not be added in its pure form to the hard soap mass. It should be made into a watery potash or soda soap, which can be mixed with the former without difficulty. However, it is important that all of these solutions are quite hot when put together, and they must be stirred thoroughly to get a uniform distribution of the Hexalin.

It hardly seems advisable to go into any detail at this point, as the methods for making Hexalin, or Methyl Hexalin soaps, as this has been covered already in a previous paper published in the American Dyestuff Reporter, May 31, 1926.

Hexalin in Lacquer

Hexalin, although an alcohol, is a solvent for nitrocellulose, but, on account of its high boiling point and its somewhat slow action on the cotton, is not recommended as the sole solvent agent, and should, therefore, be used in conjunction with the other lower boiling solvents. It is also a solvent for the various types of gums used in the lacquer industry and is a valuable addition to the present solvents, because it prevents, being the last constituent to evaporate, a separation of the nitrocellulose and the gum, and so produces an ideal film of highly glossy appearance. Its boiling

range not only prevents blushing under the most severe conditions, but also produces a better flow in the application of the lacquer and a film free from orange peel. It has also been found to promote an even distribution of the pigment throughout the lacquer where pigmented lacquers are in use.

Just a little earlier I referred to some of the new properties imparted by the use of Hexalin. An instance of this is in the case of pyroxyline lacquers. As you know, the usual solvents are various esters, such as amyl, butyl and ethyl acetate. The cotton and gums are dissolved by these solvents, and then non-solvents, such as toluol, benzol, etc., are added in order to get a lacquer thin enough for spraying purposes. We have found that by taking one of these regular lacquer combinations and adding approximately 10 per cent of Hexalin, the viscosity of the solution is greatly reduced, and this is a valuable feature where these lacquers are to be sprayed or brushed. In the case of various gums or nitrocellulose, when dissolved in Hexalin they can be thinned out to a very great extent with non-solvents without disturbing in any way the true solution.

Cyclohexanol has been found quite valuable in connection with preservation of wood, because when converted into a watery solution or emulsion it acts as a carrier for other substances used. It has also a fungicide effect of its own, and its powers of reducing surface tension and therefore inducing ready and quick penetration enable it to carry all of the materials very thoroughly into and through the products being treated. Experiments are now being conducted on a very large scale by several State experiment stations in different parts of the country to determine the extent of the fungicide and germicidal value of Hexalin in connection with plant life.

Methyl Hexalin

This is sometimes called Heptalin. Methyl Hexalin is a mixture of the three isomeric methyl cyclohexanols obtained by the hydrogenation of cresol. During the process of hydrogenation the acid character is lost entirely, the resulting product is completely neutral and the odor is also entirely changed; in fact, instead of being rather disagreeable, the resulting material has an odor rather suggesting camphor or menthol, and does not change either in long storing or by slow evaporation. Methyl Hexalin boils at between 160 and 180 deg. Cent. Its specific gravity is 0.93 at 15 deg. Cent. and the flash point, the same as with Hexalin, lies at about 68 deg. Cent. The dissolving capacity of Methyl Hexalin for fats, oils, waxes, resins, etc., is about the same as that of Hexalin.

The greatest use of Methyl Hexalin is in connection with the manufacture of soaps and other detergent compounds.

As in the case of all more highly molecular alcohols, the solubility of Hexalin and Methyl Hexalin in water is very slight—in fact, almost nil; whereas watery soap solutions are capable of absorbing large quantities of these solvents. Olein potash soap with a content of about 25 per cent of water dissolves any desired quantity of Hexalin or Methyl Hexalin, and small percentage soap solutions with as little as 5 per cent soap content still absorb Hexalin to the extent of many times this small soap content. For Methyl Hexalin the solubility in watery soap solutions is somewhat less, but nevertheless in most cases well in excess of double the soap content. A valuable fact is that Methyl Hexalin usually dissolves magnesium and lime soaps, and this dissolving capacity is maintained in a watery soap solution, so that such a preparation used where hard water conditions prevail is extremely valuable.

Specific examples of the use of Methyl Hexalin in soap were also given in the previous paper already referred to.

Cyclohexanone

Cyclohexanone is a colorless liquid with an odor resembling somewhat that of acetone. It has a boiling point of 155 to 160 deg. Cent., specific gravity of 0.95, freezing point minus 45 deg. Cent. It distills without decomposition and may be steam distilled quantitatively from its mixtures. It is non-toxic and does not attack metals. Cyclohexanone is produced simultaneously in the process of producing Hexalin.

Nitrocellulose is readily soluble in Cyclohexanone, giving clear solutions. Celluloid is also readily soluble.

Cyclohexanone is miscible in all proportions with butyl acetate, acetone, turpentine and alcohol.

Our investigations in connection with this solvent have not gone far enough yet to really develop any particular field for it in which Cyclohexanol itself would not satisfactorily do the work.

More information will probably be forthcoming as to this solvent a little later.

Hexalin Acetate

This is a colorless liquid with a typical ester-like odor. It is made by the esterification of Cyclohexanol. It has a boiling point of 175 to 185 deg. Cent., specific gravity 0.95. It is non-miscible with water and distills without decomposition.

Hexalin Acetate is a good solvent for soft and hard

natural resins and gums (including hard copals), shellac, nitrocellulose, celluloid, crude rubber, fats, oil (fixed, mineral and essential), and waxes. Hexalin Acetate is similar in its properties and actions to butyl acetate and amyl acetate, but has, of course, a higher boiling point. This ester of Hexalin has not, up to the present time, found nearly as large a use as the alcohol Hexalin itself.

Clarence C. Hubbard—You thought, perhaps, that your paper was a failure, Mr. Chairman. I want you to know that you sold the industry on your products and they will find great value in them. (Applause.)

. . . The meeting adjourned at 5.15 o'clock.

DECEMBER MEETING OF THE RHODE ISLAND SECTION

The December meeting of the Rhode Island Section of the American Association of Textile Chemists and Colorists was held jointly with the American Electro-Platers' Society and the Rhode Island Section of the American Chemical Society on Tuesday, December 14, at 8.15 p. m., in the rooms of the Providence Engineering Society.

Dr. Colin G. Fink, professor of electrochemistry, Columbia University, gave a very interesting address on "Recent Advances in Electrochemistry."

Professor Fink was at one time research engineer for the General Electric Company, the Edison Lamp Works and the Chile Exploration Company. Professor Fink originated the drawn tungsten filament and the insoluble anode for copper, and has done much work on corrosion resistant metals. His more recent contributions include the restoration of ancient bronzes.

A vote of thanks was extended the speaker.

The meeting adjourned at 9.30. Fifty-eight members were present.

A. N. DANA, *Secretary.*

Applicants for Membership

Active Membership

Barnard, Kenneth H., chemist, Pacific Mills, Lawrence, Mass. Sponsors: George A. Moran and William H. Cady.

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Skalink, Karl M., 404 North Ninth Street, Prospect Park, N. J.

Wood, L. B., 17 Montross Avenue, Rutherford, N. J.

DYES IMPORTED IN NOVEMBER

(*Continued from page 6*)

Name of Dye and Manufacturer	Quantity (pounds)
Helindone Printing Black RD Paste—(IG)	9,500
Hydron Brown G Paste—(C)	367
Hydron Brown R Paste—(IG)	1,985
Hydron Navy Blue C Paste—(IG)	300
Hydron Olive BN Paste—(IG)	800
Hydron Pink FF Paste—(IG)	1,000
Hydron Yellow GG Powder (s. s.)—(IG)	1,200
Vat Blue RSN Powder—(IG)	100
Vat Blue RZ Double Paste (s. s.)—(IG)	1,006
Vat Brilliant Blue 3G Powder (s. s.)—(IG)	800
Vat Green GG Double Paste (s. s.)—(IG)	974
Vat Orange 4R Powder (s. s.)—(IG)	1,000
Vat Pink B Double Paste (s. s.)—(B)	
Vat Pink B Powder (s. s.)—(B)	3,190
Vat Printing Brown R Paste—(IG)	2,151
Vat Printing Red G Paste—(IG)	500
Vat Yellow 3RT Double Paste (s. s.)—(IG)	1,000
Vat Yellow Brown 3G Paste—(IG)	800
Wool Vat Brown 3R Paste—(IG)	100

Mordant and Chrome Dyes

Acid Alizarine Gray G—(M)	462
Acid Anthracene Brown PG Powder—(By)	550
Anthracene Chromate Brown EB—(IG)	500
Brilliant Chrome Printing Red B—(G)	55
Brilliant Chrome Violet 3RA—(DH)	331
Chromazarine DN—(DH)	220
Chromovesuvine RA—(DH)	110
Chromoxane Pure Blue B—(IG)	400
Colonial Blue R—(DH)	110
Eriochrome Blue S—(G)	551
Eriochrome Brilliant Green G Supra—(G)	110
Metachrome Blue Black 2BX—(IG)	
Metachrome Blue Black 2BX—(A)	1,551
Metachrome Brilliant Blue BL—(IG)	100
Metachrome Olive 2G—(IG)	1,000
Metachrome Red G—(IG)	700
Modern Blue CVI—(DH)	220
Modern Olive JN—(DH)	110
Omega Chrome Brown EB—(S)	300
Radio Chrome Blue B—(IG)	500

Direct Dyes

Benzo Dark Brown Extra—(By)	1,091
Benzo Fast Black L—(IG)	100
Benzo Fast Brown 3GK—(IG)	900
Benzo Fast Eosine BL—(IG)	100
Benzo Fast Heliotrope 4BL—(By)	110
Benzo Fast Heliotrope 5RH—(IG)	100
Benzo Fast Orange 2RL—(IG)	450
Benzo Light Scarlet 5B Powder—(By)	110
Benzo Rhoduline Red B, 3B—(IG)	450
Benzoform Brown 4R—(IG)	25
Brilliant Benzo Fast Yellow GL—(IG)	200
Brilliant Congo Blue 5R—(A)	100
Brilliant Congo Violet R—(IG)	500
Brilliant Diazol Orange NJN—(CN)	881
Brilliant Diazol Orange NRN—(CN)	110
Brilliant Fast Blue 3BX—(IG)	400
Brilliant Sky Blue 8G—(By)	1,102
Brilliant Sky Blue R—(IG)	1,500
Brilliant Triazol Fast Violet BL Powder—(A)	112
Chicago Red III—(G)	2,205
Chloramine Fast Orange R Conc.—(S)	700
Chloramine Light Gray B Conc.—(S)	500
Chloramine Light Gray R Conc.—(S)	500
Chloramine Violet FFB—(IG)	300
Chlorantine Fast Blue 2GL—(I)	2,204
Chlorantine Fast Bordeaux 2BL—(I)	2,204
Chlorantine Fast Brown BRL—(I)	1,323
Chlorantine Fast Brown 5GL—(I)	2,204
Chlorantine Fast Brown 3RL—(I)	2,204
Chlorantine Fast Violet 5BL—(I)	2,645
Chlorantine Fast Violet RL—(I)	4,629
Chlorantine Fast Yellow RL—(I)	1,102
Chlorazol Fast Orange AG—(BD)	1,000
Cotton Black AC—(IG)	200
Developed Blue 3GL—(Q)	440
Developing Blue B—(IG)	300
Diamine Azo Green 3G—(C)	495
Diamine Brilliant Scarlet S—(C)	452
Diamine Catechine B—(IG)	200
Diamine Fast Brown GB—(IG)	500
Diamine Fast Brown R—(IG)	50
Diamine Fast Orange EG—(IG)	1,000
Diamine Fast Orange ER—(IG)	1,000
Diaminogene Blue GG—(C)	2,902
Diazo Black VG—(I)	220
Diazo Brilliant Green 3G Powder—(By)	2,093
Diazo Brilliant Green 6G—(By)	1,102
Diazo Brilliant Scarlet 2BL Extra Powder—(By)	440
Diazo Brown 3R—(IG)	200
Diazo Fast Blue 6GW—(I)	661
Diazo Fast Violet BL—(IG)	940
Diazo Geranine B Extra—(By)	480
Diazo Indigo Blue 4GL Extra—(IG)	500
Diazo Rubine B—(IG)	400
Diazo Sky Blue B—(By)	3,202
Diazophenyl Black V—(G)	2,205
Diphenyl Fast Bordeaux G Conc.—(G)	110
Diphenyl Fast Brown GNC—(G)	2,205
Direct Brilliant Yellow KG—(I)	110
Direct Cutch Brown GR—(I)	551
Direct Light Blue 8G—(By)	110
Direct Safranine RW—(I)	110
Fast Cotton Gray VL—(IG)	500
Formal Fast Black G Conc.—(G)	220
Half Wool Blue 3R—(IG)	2,047
Minaxo Light Pink BX, BBX—(IG)	400
Paper Red A Extra—(IG)	500
Plutoform Black BL—(IG)	100
Rosanthrene Orange R—(I)	661
Universal Blue C—(IG)	25
Universal Brown C—(IG)	25
Universal Gray C—(IG)	25
Universal Green C—(IG)	25
Universal Heliotrope C—(IG)	25
Universal Jet Black C—(IG)	25
Universal Leather Brown C—(IG)	25
Zambesi Black D—(IG)	1,000
Zambesi Black V—(IG)	500

Dyes for Artificial Silk

Blue Extra Paste—(IG)	100
Cibacete Scarlet G Paste—(I)	220
Dispersol Yellow 3G Paste—(BD)	106
Duranol Black Paste—(BD)	474
Duranol Blue G Paste—(BD)	168
Duranol Orange G Paste—(BD)	50
Duranol Red BB Paste—(BD)	106

Name of Dye and Manufacturer	Quantity (pounds)
Duranol Violet 2R Paste—(BD)	156
Ionamine A—(BD)	100
Ionamine Red KA—(BD)	100
Setacyl Direct Blue G Powder—(G)	1,116
Setacyl Direct Blue R Powder—(G)	2,204
Setacyl Direct Orange 2R Powder—(G)	727
Setacyl Direct Red B Powder—(G)	551
Setacyl Direct Yellow R Powder—(G)	1,763
Yellow R—(IG)	50

Basic Dyes

Acridine Scarlet J—(DH)	165
Brilliant Acridine Orange 3R—(DH)	220
Rhodamine 6GDN Extra—(IG)	5,000

Sulphur Dyes

Immedial Brown W Conc.—(IG)	500
Indo Carbon SN—(IG)	1,500
Pyrogene Green GK—(I)	1,323
Thiogene New Blue BL Conc.—(M)	550
Thional Brilliant Green GG Conc.—(S)	275
Thionol Green B—(BD)	6,256
Thionol Green 2G—(BD)	2,240
Thionol Yellow GR—(BD)	1,947

Color-Lake Dyes

Hansa Yellow GSA Powder—(IG)	2,000
Helio Bordeaux BL Powder—(IG)	835
Helio Fast Carmine CL—(IG)	100
Helio Fast Rubine LBK Powder—(IG)	400
Helio Red RMT Extra Powder—(IG)	1,061
Stone Rubine G Powder—(IG)	100

Unclassified Dyes

Grasol Blue R—(G)	22
Grasol Red G—(G)	22
Grasol Scarlet G—(G)	22
Luxine Violet 5RN—(DH)	11
Navy Blue KWSR—(IG)	250
Purple DH—(DH)	11
Whitex Washing Blue—(Eze Mfg. Co.)	6,800
All other—(Q)	3

LIST OF APPRAISEMENTS OF COAL-TAR PRODUCTS WITHIN PARAGRAPHS 27 AND 28 OF THE TARIFF ACT OF 1922

The following supplemental list contains the month of entry, the name of the product within paragraphs 27 and 28, together with the designations as "C" (for competitive) and "NC" (for non-competitive), which indicates the appraisement basis for the assessment of the ad valorem duty in paragraphs 27 and 28 of the Tariff Act of 1922.

The ad valorem rate for competitive dyes is based on the American selling price, as defined in Subdivision (f) of Section 402 of Title IV; the ad valorem rate for non-competitive dyes is based on the United States value, as defined in Subdivision (d) of Section 402 of Title IV of the Tariff Act of 1922.

This list contains the appraisements received since the publication of the October list for the Port of New York, beginning with January, 1926.

JANUARY

Acid Violet 10B	C
Azo Orseille BB	NC
Developing Black ED 70%	C
Diamine Fast Scarlet GG 60%	C
Erythrosine A	NC
Helindone Fast Scarlet B Paste	NC
Helindone Pink IB Double Paste 20%	NC
Helindone Printing Black RD Paste 20%	NC
Hydron Yellow Brown G Paste	NC
Indanthrene Blue GCD Double Paste	C
Indo Carbon SN	NC
Methylene Heliotrope Extra Strong	NC
Nako Black ST	NC
Oxydiamine Blue BG 80%	NC
Thio Indigo 3B Powder	NC
Thio Indigo Orange R Paste	C
Thio Indigo Scarlet 2G Paste	NC
Vat Brown 2G Paste	NC
Vat Green 2G Double Paste	NC
Vat Red Violet RRK Paste	NC
Vat Violet BN Paste	NC

FEBRUARY

Acid Rhodamine 3R 48%	C
Benzo Fast Blue L 36%	NC
Chlorantine Red 8BN 54%	NC
Chrome Printing Orange 2R Powder 79%	NC
Ciba Red R Paste 20%	NC
Cibanone Blue 3G Paste 10%	NC
Cibanone Orange R Powder 76%	NC
Cloth Fast Red B 60%	C
Cloth Fast Red 3B 77%	C
Cloth Fast Red B 73%	NC
Cloth Fast Yellow G 40%	NC
Kiton Fast Yellow 3G 81%	NC
Kiton Fast Yellow 3G 77%	NC
Nephto Chrome Violet R 19%	NC
Patent Phosphine G 87%	C
Patent Phosphine GG 81%	C
Thio Indigo Scarlet 2G Paste	NC
Victoria Blue B 80%	C
Xylene Milling Blue BL Conc	NC

MARCH

Alizarine Blue AS	NC
Indocyanine B	NC

APRIL

Alizarine Red S Powder	C
Anthra Rubine B Powder	C
Developed Brilliant Scarlet 2BL Extra Powder	NC
Developed Pure Blue B Powder	NC
Diaminogene Blue NA	C
Rhodamine B Extra	C
Thio Indigo Rose BN Extra Paste	NC
Vat Blue 3G Powder	C
Vat Green 2G Double Paste	NC
Vat Violet BN Paste	NC

MAY

Alizarine Blue AS Powder	NC
Alizarine Blue SKY Powder	NC
Brilliant Indigo BASF Paste B Fine 20%	NC
Ignamine Orange RR 70%	NC
Madder Lake VN 14 Powder	C
Metachrome Blue Black 2BX	NC
Thional Brilliant Blue 6BS Conc	C

JUNE

Alizarine Blue AS	NC
Alizarine Blue SKY	NC
Alizarine Blue WS	C
Ciba Pink BC Powder 68%	NC
Cibacete Navy Blue 3R Powder	NC
Cibacete Orange 3G Powder	NC

Cibacete Scarlet G Powder	NC
Cibacete Yellow 2R Powder	NC
Cibanone Blue GCD Double Paste	C
Cyanole Extra	NC
Diamine Azo Brown 3G	NC
Diaminogene Extra	C
Diaminogene GG Powder	NC
Grelanone Olive B Powder	NC
Pyrogene Green GK 64%	NC

JULY

Anthra Rubine B Powder	C
Anthraquinone Violet	NC
Azur Blue Powder	C
Benzyl Fast Blue BL 45%	NC
Benzyl Fast Blue GL 26%	NC
Brilliant Acid Blue FF 100%	NC
Brilliant Milling Blue B	NC
Brilliant Silk Blue B 59%	C
Chlorantine Fast Blue 2GL 36%	C
Chlorantine Fast Brown 3RL 79%	C
Chlorantine Fast Violet 5BL 30%	NC
Ciba Red R Paste 20%	NC
Cibanone Blue G Paste 20%	C
Cibanone Blue 3G Paste 10%	NC
Cibanone Blue GCD Double Paste 16 2/3%	C
Cibanone Orange R Paste 10%	NC
Cibanone Orange 6R Powder 85%	C
Color Lake 1054	C
Cotoneral A Extra 60%	NC
Diaminogene NA Powder	C
Diazo Fast Blue 6GW 90%	NC
Direct Sky Blue 8G Extra Powder	NC
Kiton Blue A 82%	C
Kiton Fast Red 4BL 79%	NC
Naphto Chrome Violet R 19%	NC
Neolan Blue GG 40%	NC
Patent Blue A Powder	C
Patent Phosphine G 87%	C
Patent Phosphine M 86%	NC
Pyrogene Green 3G 78%	C
Triazol Fast Brown 3GL	C
Vat Blue RC Paste	C
Vat Brilliant Violet R Paste	NC
Victoria Blue R Base 85%	NC

AUGUST

Acid Alizarine Gray G	NC
Acid Milling Yellow G Conc	NC
Alizarine 20% Cow Brand	C
Alizarine 20% Ear-Ring Brand	C
Alizarine 16% Ear-Ring Thick Paste	C
Alizarine 20% Thin Paste	C
Alizarine Blue AS Powder	NC
Alizarine Blue JR Powder	NC
Alizarine Sapphire Blue B 58%	C
Alizarine Sapphire Blue SE 72%	C
Chloramine Red B	C
Chloramine Red 3B	C
Chlorantine Fast Gray B 98%	NC
Chlorantine Fast Yellow 4GL 79%	C
Chrome Orange R	NC
Chromocitronine R	NC
Developed Pure Blue B Powder 100%	NC
Diaminogene GG	NC
Indigosol O4B	NC
Indigosol Orange HR	NC
Indigosol Pink HR Extra	NC
Kiton Blue L 60%	C
Kiton Fast Red 4BL 79%	NC
Modern Azurine 5G	NC
Modern Blue CVI	NC
Neolan Blue B 46%	NC
Neolan Blue G 42%	NC
Neolan Blue GG 52%	NC
Parasulfon Brown G 70%	NC
Rhodamine B Extra 90%	C
Rhodamine B Extra Powder 500%	C
Rosanthrene R 20%	C
Vat Brown 2G Paste 12½%	NC
Xylene Milling Blue GL Conc	NC

SEPTEMBER

Alizarine Light Blue B	C
Alizarine Light Blue B Conc	C
Alizarine Light Violet RS Conc	NC
Alizarine Sapphire Blue SE 72%	C
Anthracyanine S	NC
Brilliant Chrome Violet 4B	NC
Chloramine Brilliant Red 8B Conc	NC
Chloramine Red 3B	C
Chromazurine DN	NC
Chrome Printing Orange BW	NC
Chrome Violet CG	NC
Chromocitronine 3R	NC
Chromorhodine 6GN Extra	NC
Cyanole Extra Powder	NC
Developed Pure Blue B	NC
Diamine Briliant Violet B	C
Diaminogene Blue GG	NC
6 Soloid M/S Fuchsine 0.1 gm. Basic	NC
Indigosol AZG	NC
Indigosol O4B	NC
Indigosol Red HR	NC
Indigosol Scarlet HB	NC
Indigosol Violet AZB	NC
Indigosol Yellow HCG	NC
Madder Lake 71 Extra Powder	C
Modern Blue CVI	NC
Modern Gray PS	NC
Modern Violet	NC
Neolan Orange R 40%	NC
6 Soloid Neutral Red 0.1 gm. M/S	NC
6 Soloid Romanowsky Stain 0.015 gm. M/S	NC
Thional Brilliant Blue 6BS Conc	C
6 Soloid Toison Blood Fluid M/S	NC
Viridine Lake 1026 H Powder	C
Whitex Washing Blue	NC

OCTOBER

Acid Navy Blue MB	NC
Bismarck Brown S	NC
Chloramine Fast Violet R	NC
Chloramine Red B	NC
Chloramine Sky Blue FF	NC
Chromovesuvine RA	RA
Modern Green N	NC
Resorceine Brown B	NC
Trisulfon Brown 2G	NC
Trisulfon Brown MB	NC
Trisulfon Violet B	NC
Victoria Violet 4BS	NC

AMERICAN
DYESTUFF REPORTER
SAMPLE SWATCH QUARTERLY

Devoted to the use and application of dyestuffs and the mechanical equipment incidental thereto.

LOUIS A. OLNEY
PROFESSOR OF CHEMISTRY AND DYEING, LOWELL TEXTILE SCHOOL
Directing Editor

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OUTGROWING ROUTINE IN THE MILL LABORATORY

THE mill chemist should endeavor to work in advance of his daily routine; that routine should not hinder him from giving some time to the study of the larger technical problems lying outside his immediate duties. This is one of the inspiring thoughts in Alan Claflin's article, "Nineteenth Century Chemistry and Twentieth Century Needs," appearing in this issue. It is a thought that should appeal to chemists who have ideals but who are dissatisfied because they have apparently come to rest on the dead level of mere mill worker.

The shortest way out of the routine rut is that suggested by Mr. Claflin. One must be able to systematize his regular schedule so that a large part of the work can be handled by an assistant. This should give the chemist ample time for studying the more fundamental problems of textile chemistry—problems, whenever possible, related to his own mill's type of work.

The mill management may frown upon special studies of this nature, on the score that they bring no tangible returns. This attitude is wrong. Perhaps a simple explanation of how the behavior of wool toward various acids may determine changes in dyeing or bleaching methods, for instance, might help to convince those who do frown that such researching has a practical end.

But the most stubborn opposition to this idea of working ahead of routine is usually the chemist's own reaction to it—or rather, his total lack of reaction. Mill chemists, being human as a rule, postpone things, such as research work. Then "days are lost lamenting over days," as the poet Goethe sang; and lamenting, unfortunately, accomplishes nothing. Chemists who are continually saying "some day" will not turn in very many research reports. They must first learn three things: First, to follow a definite plan of study; second, to allow nothing to interfere with that plan, and third, to devote a fixed period—six months or a year—to the study of one or two problems until those are solved. To-day the plan should be laid out, to-morrow the work begun; that way lies the road to results in working ahead of routine.

One fact, however, must impress the chemist before he will be attracted by this idea. It is this: that since a mill laboratory offers so many open avenues for research, the industrious man should be able steadily to increase his value, and what is more, to receive that value. Mills may not appreciate to-day the full worth of the man in their laboratory; but mark these words—they will to-morrow, if the chemist will strive to make his position something more than that of a plodding routine worker.

Recognition of what the chemist *can* do for the textile mill—not so much of what he is doing now—is growing day by day, and those who impatiently leave for more attractive rewards in other fields shall regret their lack of foresight. The chemist has only begun to serve the textile industry. His greatest work lies ahead and he will be ready for it as soon as he outgrows routine.

DYE RESEARCH IN WASHINGTON

THE Government's research work in color chemistry has evidently produced results that justify its value to industry. An appropriation of $72,921 for the Color Laboratory of the Bureau of Chemistry is included in the latest appropriation bill of the Department of Agriculture.

The Color Laboratory has made a number of valuable scientific studies of the chemistry of dyestuffs. Some of its reports, notably those on dye analysis and identification by Holmes, have appeared from time to time in The REPORTER. Together these represent work in a highly specialized field of technical research that is not by any means well known. The results have undoubtedly added to our knowledge of the constitution and properties of dyes and to that extent have directly benefited both the dyestuff and textile industries.

In the past year or two the marketing of chemicals in this country and abroad has been the subject of study by the Department of Commerce, which through its chemical division supplies the chemical industry with much valuable commercial information. Why not more active co-operation between the dye industry and the Color Laboratory, for the advancement of *technical* knowledge? The Color Laboratory might be better developed as a research unit if the industry showed more interest in it.

A THOUGHT TO RELATIONS

SOME of our readers, when they come to the end of this brief piece, may wonder why it does not bear some such title as "In 1927." We have purposely avoided labeling it with anything that might remotely suggest a survey of business conditions. We have not the slightest intention of adding our mite to the lengthy columns of business reviews that have clogged the pages of the press

the country over. The story of our progress and prosperity in 1926 has been told ten thousand times in the past few days by business analysts much more capable than we presume to be.

Annual resumés and predictions of business serve a very worthy purpose—never question that. But they are frequently dull, their optimism is usually overdone, and by their very number they confuse rather than guide the bewildered business man. They talk in broad generalizations or else in boresome detailed statistics, in gross tonnages and carloadings, in corporation profits, production levels, dividends and bank clearings. They pile up figures that becloud the more *human* aspects of the year's activities. Dealing in big movements of markets and money, they lose sight of the human relations in business.

In beginning another year business men can scarcely turn their thoughts to a more interesting subject than this one of the relations among men and groups of men in trade and industry. The relationships existing in our own industry, between employer and employee, between superintendent and dyer and chemist, between dyestuff manufacturer and demonstrator and mill man, are really a decisive factor in determining how far we shall advance and prosper during this year. For no matter how prosperous 1927 or any future year may be for business in general, the welfare of the textile industry and of the dyestuff industry would not be noticeably improved if, by some misfortune, a strain should occur in their mutual relations or within their own ranks.

Think about that for a minute. Try to realize how much depends on the kind of relation you bear to your own work and to other men and their work and interests. Regard your own interests as only one element in the elaborate business system of your industry. In taking this slant appreciate the fact that your personal success this year will depend largely on how you serve those you work for, and those who work for you. If you are in the dyehouse or laboratory it will depend on how intelligently you strive to improve your work; upon the attitude you hold toward the mill and toward those in your department; upon whether or not you have learned properly how to serve. If, on the other hand, you are selling dyes, your advancement during this year will depend on how diligently you strive to spread good-will for your firm and its products, and upon how truly you represent the ideals of that firm. It will depend upon your spirit of helpfulness toward the dyers with which you come in contact, upon the confidence they have put in you, and upon the many similar human relations that enter into your day's work.

The foregoing is intended only to be suggestive. It offers but a bare hint of how fruitful this subject is for further consideration, and how timely it is at this season, when one year has just passed into limbo and another looms ahead. To maintain last year's record, improve your business relations during 1927.

SILK ASSOCIATION HOLDS ITS ANNUAL BANQUET

Fourteen hundred men and women of the silk industry attended the fifty-fifth annual dinner of the Silk Association of America in the grand ballroom of the Hotel Astor on Saturday evening, January 8. This notable event marks the closing celebration of each year in the silk industry.

George A. Post, president of the association, delivered the address of welcome, outlining the principal achievements and activities in the industry during the year. He told his audience that the present volume of production in the silk industry is the wonder of all the world. Chief among the many important advances made, Mr. Post said, was the completion last year of methods and standards of measuring raw silk.

Mr. Post further assured his audience that the association's efforts to secure more and better silk from China were materializing. "I think we have nothing to fear politically from communism in China," said Mr. Post, adding "the Chinese people of the South are very progressive, and those persons who are acquainted with the situation think it is temporary and only a means to an end."

The dinner was enlivened with music by the Roumanian orchestra, and parodies were sung on the troubles and joys of the silk business. Following the dinner was an entertainment of vaudeville numbers arranged by the dinner committee of which H. T. Fleitmann was chairman.

AUGUST MERZ NEW PRESIDENT OF S. O. C. M. A.

Charles Mace, Secretary

At the annual meeting of the Synthetic Organic Chemical Manufacturers' Association held in the Hotel Commodore, August Merz, vice-president of Heller & Merz Company, was elected to succeed Dr. Chas. H. Herty as president of the Association. Dr. Herty, it will be recalled, recently resigned the office which he had held since the Association was organized, and is now associated with the Chemical Foundation.

An amended constitution was adopted calling for the election of a president, treasurer and secretary by the board of governors, the president to be selected from among representatives of member firms and the secretary to be a paid officer and executive head of the association offices.

Charles A. Mace has been appointed as secretary to the association and will assume his duties on February 1. Through long and thorough experience in the textile and dyestuff manufacturing industries, Mr. Mace is particularly well qualified for the position defined by the new amendment.

Technical Notes from Foreign Sources

Action of Light on Cotton

The production of oxycellulose in cellulose during exposure to light is preceded by the formation of "photocellulose," a substance which has similar properties. Thus this substance will give a yellow coloration with sodium hydroxide solutions or phenylhydrazine, and it also has a reducing action towards silver salts or Fehling's solution. The increased affinity of exposed cotton for Methylene Blue is not directly due to the presence of photocellulose. Cotton is not deleteriously affected by visible light, but only by ultra-violet light such as that emitted by a mercury vapor lamp, wave length approximately 350 mu. The action of light on cotton is independent of the presence of oxygen, either external or occluded, or moisture, and since there is no accompanying change in weight, the resulting deterioration or formation of photocellulose is not the result of oxidation.

Photocellulose has the formula $C_5H_{10}O_5$ and its formation in the exposed cotton may be followed by an adaptation of the method in which potassium permanganate is employed. In bleaching cotton by exposure to sunlight in meadows the natural yellow to brown pigment is destroyed by visible light, but the cellulose is simultaneously affected by the ultra-violet light, 1 to 2 per cent of photocellulose being found in the cotton fabric thus exposed for forty-five days. The deterioration of cotton by light may be prevented by the presence of suitable light-absorbing pigments, but Anthracene Yellow GC and Chrysoidine have been found unsatisfactory for this purpose. (Melliand's Textilberichte, 1926, volume 7, pages 617-18.)

Activin in Volumetric Analysis

Crystalline activin, sodium para-amino chloro toluene sulphonate, is a satisfactory oxidizing agent for use in the volumetric analysis of tartar emetic and antimony lactates as used for the mordanting of cotton, and of sodium formaldehyde hydrosulphite. During oxidation, activin is decomposed thus:

$$C_6H_4CH_3.SO_2NClNa + H_2O =$$
$$C_6H_4CH_3SO_2NH_2 + NaCl + O.$$

In the analysis of tartar emetic, a mixture of 25 c.c. of a 1.6 per cent solution of the sample of tartar emetic and 20 c.c. of a 2 per cent solution of sodium bicarbonate is titrated with a tenth normal solution of activin 14.1 grams per liter) using starch-potassium iodide as an indicator. In the analysis of sodium formaldehyde-hydrosulphite, a 0.4 per cent solution of the sample is titrated directly with a tenth normal solution of activin, using starch-iodide as an indicator.

The results obtained with the aid of activin agree very closely with those obtained by the usual methods using iodine, titanous chloride or hydrogen sulphide. Aqueous solutions of activin do not deteriorate when protected from sunlight during storage; appreciable deterioration is produced by sunlight. Commercial activin is sufficiently pure for volumetric analysis after filtration of its aqueous solution, but it may readily be purified by crystallization from its aqueous solution. (Melliand's Textilberichte, 1926, volume 7, pages 850 to 851.)

Wetting-Out Agents for Textile Materials

Determination of the efficiency of wetting-out agents by methods dependent on the rate of sinking of yarn or fabric in an aqueous solution or the spread of a solution along a horizontally suspended thread are considered unsatisfactory because they are subject to the disturbing influences of air bubbles occluded in the textile material, and the humidity of the surrounding atmosphere respectively. The relative wetting-out powers of various proprietary substances were determined by comparison of the amounts of solution absorbed by similar pieces of fabric, 5 by 6 centimeters in size, when immersed for ten seconds in 0.2, 0.4 and 0.6 per cent solutions of the wetting-out agents, and then allowed to drain for fifty seconds after withdrawal. The wetting-out powers of Oranite powder, Nekal, Avivan, Avirol KM, Diffusil N, Koloran K, Marseilles soap, Monopole soap, Turkey Red oil (50 per cent fat) and Tetracarnite, decreased in the order named. The first three agents named are said to be alkyl derivatives of naphthalenesulphonic acids.

The article also contains a detailed discussion of the mechanism of the wetting-out process and the manner in which it can be improved. It is shown that the limiting surface tension of the solid to the liquid at the points where they come in contact with one another is one of the important factors that determine the effectiveness with which the wetting-out is accomplished. The capillary attraction of the solid for the liquid and the surface tension of the liquid are also important. It is shown that wetting-out agents generally contain a fat solvent of some sort and also a substance that tends to reduce the surface tension of the liquid and thus increase the capillary attraction of the solid for the liquid.

For further details see Melliand's Textilberichte, 1926, volume 7, pages 851-854.

Dyeing Cellulose Acetate

Oxidation shades from fawn to full black are produced on cellulose acetate without impairing the handle or luster, by first applying a free amino base which has been solubilized or dispersed in water, then preferably rinsing and impregnating the goods with a solution of suitable oxidizing and catalytic agents, drying without rinsing, and "aging" by exposure to warm moist air or steam. Alternatively, the amino base may be applied in the form of its water-soluble salts

For example, in order to produce a full black, ¾ of a pound of para-aminodiphenylamine is intimately mixed with 6 pounds of Turkey Red oil by heating at a temperature of 80 deg. Cent., and the mixture is dispersed in 25 gallons of soft water at a temperature of 80 deg. Cent. Ten pounds of cellulose acetate yarn are worked in the liquor as for dyeing for approximately two hours, and then rinsed off. The yarn is then impregnated with about its own weight of a solution containing 2 parts of gum tragacanth, 8 parts of chromium chloride, 4 parts of aluminum chloride, 3 parts of cupric chloride and 60 parts of sodium chlorate, each separately dissolved, and made up with water to a total of 1,000 parts. The impregnated goods are preferably dried at a moderate temperature and "aged" for five minutes in a steam ager, then washed off in hot water or a very dilute formic acid solution. (British Patent No. 255,962.)

Damaged Cotton Hairs Under the Microscope

A microscopical examination was made of damaged cotton hairs by the Congo Red test and the swelling test of Fleming and Thaysen. The cuticle of a cotton hair stains with Congo Red to a lighter shade than the cellulose encased by it. Consequently damage to the cuticle which exposes the cellulose can be detected by observation of the stained hair under the microscope.

The cotton is wetted out, swollen in an 11 per cent sodium hydroxide solution, rinsed, stained in Congo Red (2 per cent solution), and mounted in 18 per cent sodium hydroxide solution. The final swelling causes the cuticle to crack spirally if the hair is sound, so that unstained cellulose shows up underneath a faint pink band of cuticle. With a hair damaged by mechanical means, the cellulose will already have been exposed and will have become deeply stained, presenting the appearance of a bruise.

Damage by heat is shown by the appearance of spiral bands which become very numerous as the heating is prolonged, while badly damaged hairs fail to swell properly in the final sodium hydroxide solution. Mildew damage often results in deep staining throughout, but actual rupture of the cuticle may not be observed. Cotton hairs damaged by sulphuric acid, however, do not give a characteristic appearance on staining, but if the damage is severe it will be observed that the hairs do not swell to the rod shape in the caustic soda.

A test developed by Fleming and Thaysen for detection of damage by micro-organisms (see Berichte, 1920, page 263 A; 1921, page 764 A) has been examined on the same material (Sakel cotton) as tested by the Congo Red method. The conclusion is drawn that the two tests vary in efficiency according to the material. For detecting small amounts of mechanical damage such as might occur to cotton in spinning process, the Congo Red test appears to be the more promising. (Journal Textile Institute, 1926, volume 17, pages 396-404 T.)

Immunization of Vegetable Fibers

Cotton immunized by means of para-toluenesulphochloride has a harsher and fuller handle than normal cotton, the individual fibers contracting in length and swelling with almost complete elimination of the lumen. Immunized cotton has a resistance to water about equal to that of cotton waterproofed by means of aluminum acetate and soap, and is less hygroscopic than normal cotton. Immunized cotton has a strong affinity (proportional to the degree of immunization) for basic dyestuffs, and its dyeing properties are similar to those of oxycellulose and cellulose acetates and benzoates.

Immunization causes an increase of weight of the fibers of 2 to 12 per cent. Dyed yarn has increased fastness after immunization, probably due to a contraction of the active surface of the fibers. Cotton immunized by means of para-toluenesulphochloride is more resistant to alkalies than the cellulose esters of aliphatic fatty acids. Immunized cotton materials are resistant to the usual processes for preparing cotton for dyeing and printing, although plate-singeing and other dry treatments at temperatures exceeding 120 to 125 deg. Cent. should be avoided, since they produce partial decomposition.

Alkalies produce swelling and saponification, but rapid processes of mercerization or "philanizing" have no harmful effect. Local immunization of cotton fabrics may be effected and the resulting fabric then dyed in two colors Immunization does not proceed uniformly within vegetable fibers, since the esterified portions may be extracted with suitable solvents, and the insoluble residue shown to have an affinity for direct dyestuffs. There is a possibility of immunizing cellulose silks during spinning and coagulation. (Textilberichte, 1926, volume 7, pages 765 to 770.)

Fixation of Basic Dyes

The fixing agents mentioned in German Patents No. 399,898 and 400,776, that is, the sulphurized phenols, used either in the form of alkali salts as there described, or in the newly discovered form of colloidal solutions of the free phenols, are applied to the aftertreatment of the colored fabric in the presence of dispersing agents, such as soaps, proteins, sulphonic acid and the like. The ad-

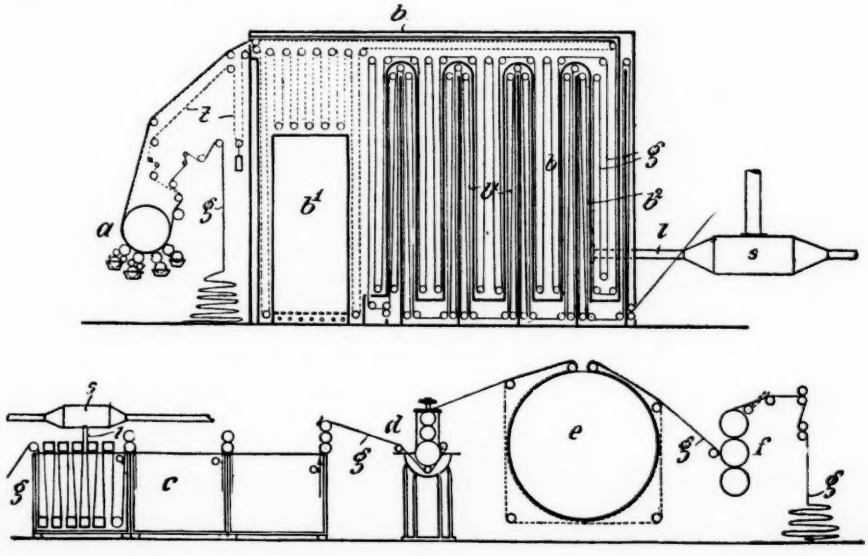
dition of the dispersing agent causes a diminution of the affinity of the phenols for the fiber without affecting the lake formation between basic dyestuff and phenols. The pattern on the fabric is therefore fixed fast to washing, while the ground is colored only pale yellow. (German Patent No. 430,679.)

Steaming Apparatus for Aftertreating Printed Fabrics

In accordance with the process covered by German Patent No. 425,166, the current of steam is led through the steamer, into the drying chamber and thence into the calenders, whereat the condensate flows off as wash water through the washing equipment. The cloth is accordingly finished with one and the same current of steam in apparatus interconnected, and this has the effect of increasing to a considerable degree the capacity and the economy of the entire installation.

This installation is shown in diagrammatic form in the accompanying illustration. The cloth is seen at *g*. It passes through the printing machine which is indicated at *a* and thence it passes into the drying chamber *b*. A box-shaped steaming apparatus is built into this chamber which is shown at b^1, The chamber contains as well the steaming chamber b^2, which consists of a number of vertical partitions between which the cloth is made to pass over suitable rollers and guide devices. The container *s* holds the various chemicals that are used in aiding the fixing of the color on the fabric, and these agents may be either solid, liquid or gaseous in form.

The dried and steamed finished cloth *g* now passes into the wash bath *c* to which the suitable chemicals are likewise fed from a container *s*. After the cloth has left the washers, it passes through a sizing apparatus *d* which is fed with starch, then squeezed between squeeze rollers and finally passed over the drying cylinder *e* and the calender rolls *f*. The three apparatus *d*, *e* and *f* are heated by the steam which comes from the chamber *b*.



Printing with Metallic Powders

A paste employed for the purpose of printing fabrics with metallic powders is composed in the following way: Twenty kilograms of white glue of good quality are boiled with 80 liters of water for one hour under a pressure of half a kilogram and then treated with alkali overnight. The solution gelatinizes on cooling. The product has a definite melting point, which lies between 27 and 35 deg. Cent., according to the duration of digestion and the quality of the glue. The customary grades of this product melt at low temperatures. The resulting glue can change from the gelatinous to the liquid condition and vice versa, without producing any alteration in the critical temperature. This is a distinct physical characteristic of the substance.

It is necessary to use the printing paste, which consists of a mixture of glue and gold leaf, at the critical temperature, the printing being carried out with the aid of carefully heated rollers or plates. The rollers are best heated to the proper temperature before printing. The printed designs are rendered fast to soaping by passage through vapors of formaldehyde. Subsequent calendering gives the printed fabric the appearance of being covered with gold leaf.

It has been found that the metallic powder suspended in the glue has a tendency to settle out. This difficulty can be counteracted by increasing the viscosity of the glue solution Very highly concentrated glue solutions are obtained by prolonging the digestion period and increasing pressure. The gelatinizing point of these solutions can be regulated at will.

In metallic printing of fabric it is necessary that temperature be maintained at 30 to 40 deg. Cent. in order to produce printed designs fast to rubbing. The best results are obtained by digesting 600 kg. of glue with 400 kg. of water for a period of eight hours under a pressure of 2 kg. The printing pastes, which are obtained by mixing the metallic powders with this mass, are permanent and can be used without any difficulty.

It has also been found that these pastes can be advantageously printed simultaneously with Algol, Helindon and Indanthrene dyestuffs on a colored ground, which can be discharged with hydrosulphite. The printed materials are then fixed with the aid of formaldehyde vapors, and then washed and soaped.

Other processes are employed for obtaining these printing pastes. In these such substances as albumen, damar

resin, boiled linseed oil, varnish, gum tragacanth, camphor oil and the like are employed. Quite a number of substances have been recommended for making up the metallic powder printing paste without any of them being able to solve the problem up to the present time. There are some that give results not sufficiently fast to washing and rubbing, and others, satisfactory from these standpoints, but which attack the cloth on which they are used and at times the printing rollers themselves, in that they coagulated with water. Still others are too expensive for common use.

The glue or gelatine process seems to be the most suitable of all. The thickening agent, also used in making the paste, is prepared in the following manner: Six hundred parts of glue are gradually added in several portions to 400 parts of hot water, in a suitable autoclave. When everything has been dissolved, the contents are brought up to the boiling temperature, the autoclave shut and the digestion continued for a period of eight hours at a pressure of 2 kg. with constant stirring. Then the contents of the autoclave are discharged and the solution allowed to cool.

A brownish-colored product is obtained of the consistency of a thick rubber solution. This thickening compound reacts neutral towards the common reagents and gave the biuret reaction. It is precipitated by alcohol and ether and coagulated with formaldehyde-like gelatine. It is absolutely stable.

The printing must be carried out at an elevated temperature in order to attain the desired fluidity of printing paste. After printing, the goods are treated with formaldehyde vapors, carefully washed and soaped and calendered. (Deutsche Faerber Zeitung, 1926, page 1012.)

Dyeing Rubbing-Fast Shades on Animal Fibers

For enhancing the fastness to rubbing of dyeings on animal fibers, there is added to the dye bath, fuller's earth, kieselguhr, loam, kaolin and like substances which are adapted to render harmless impurities such as residual grease and lime soaps derived from the fiber or the dyestuff. The process is applicable to Diamond Black F, acid dyestuffs, the ester salts of vat dyestuffs such as obtained in British Patent No. 186,057. It may also be employed with ordinary wool, unwashed wool, skinner's wool and cowhair.

Before use, the fuller's earth and the like may be treated with acid, or the amount of acid in the dye bath may be adjusted to compensate for the acid consumed in neutralizing the added fuller's earth.

In examples, the goods are dyed in a bath which contains Indigosol D, Hydrosulphite NF, fuller's earth and acetic and formic acids, the bath being raised to the boiling point which is continued after the addition of sulphuric acid. Thereafter, the goods are washed and oxidized in a cold bath which contains sulphuric acid and alkali chromate or nitrite. A dye liquor made up with Diamond Black F, fuller's earth and acetic acid is employed, and in this the goods are boiled, boiling being continued after the addition of sulphuric acid, and developed after the addition of alkali chromate. (British Patent No. 255,501.)

Fillers

A filler in paste or powder form for pigment colors, and the like comprises organic materials (excluding basic dyestuffs) fixed or bound by colloidal suspension of color fixing earths such as fuller's earth, bentonite, green earth or white earth. Organic materials suitable for use comprise vegetable, mineral or animal oils or fats, paraffine wax, Turkey Red oil, or organic materials containing amino or hydroxyl groups. The filler may be dyed with basic dyes.

In an example a colloidal aqueous suspension of fuller's earth is treated with mineral oil and either dried or precipitated with a little aniline oil or aniline salt. (British Patent No. 252,416.)

THREE NEW CAMEL DYES

Three new colors have been developed in the laboratory of John Campbell & Co., and recently placed on the market as additions to this manufacturer's series of Camel Dyes. These new colors are Alizarine Cyanine Green G Extra, Amidine Chrome Brown BS and Amalthion Bordeaux R. Of the last-named product a very concentrated form has also been produced under the name Amalthion Bordeaux R Extra Conc.

B. P. Ducas Company, Inc., manufacturers and importers of colors, chemicals and dyestuffs, announces that C. E. Moss has joined its sales force.

NEW RAYON SIZING CHEMICAL

An interesting leaflet has been issued by Stein, Hall & Co., describing the properties and use of Raygomm, a product recently perfected by its laboratories for giving strength and body to lustrous material, such as rayon, silk, mercerized cotton and similar goods. It is used in sizing cotton and rayon warps and for obtaining light finishes. This product, according to the announcement, does not lump or clot at low temperatures, assuring more even sizing of the warp. Because of its transparency feature, it is claimed to be specially valuable for colored goods.

Albert Jaeger, formerly dyer at the J. E. Kenworthy Company, Warren, R. I., is now general manager of the Thies Dyeing & Processing Company, of Central Falls, R. I.

Announcement is made by the Kalbfleisch Corporation of the appointment of Joseph D. Lowery as assistant sales manager of the heavy chemicals division of that company. Mr. Lowery assumed the duties of this position on the first of January.

RECENT LITERATURE

Effect of Dry Cleaning on Silks—a Comparison of the Effect of Dry Cleaning and Some Service Conditions on the Strength of Silk. By M. H. Goldman, C. C. Hubbard and Charles W. Schoffstal. Technologic Papers of the Bureau of Standards, No. 22. 30 pages, illustrated.

THIS important pamphlet outlines in some detail the tests made on samples of weighted and unweighted silk to determine the extent of deterioration caused in the dry cleaning processes. Two of the authors, M. H. Goldman and C. C. Hubbard, are well known as research associates of the National Association of Dyers and Cleaners.

The members of this association were desirous of obtaining adequate information of any effects which the process of dry cleaning would have on silks, especially weighted silks. Although primarily interested so that proper safeguards could be made against the numerous claims to which they were being subjected, they also were anxious to make such changes in the process as would be shown expedient if the research work disclosed that the dry cleaning process was at fault. Accordingly, the work was carried on by the research associateship of this association established at the Bureau of Standards.

Occasionally in cleaning a lot of garments it has been found that one of them will be more or less tendered. The other silk fabrics, although subjected to the identical dry cleaning process at the same time, are unharmed. Microscopical analyses of the damaged portions in each of the instances submitted by cleaners for study showed acid burns, and these were confirmed by chemical analyses, which gave an acid reaction and usually disclosed chloride ions. Tin weighting was found in each instance.

The conclusions reached by the investigation are abstracted in the report as follows:

> The study of tin-weighted and unweighted samples of silk after various treatments and exposures to sunlight and storage at standard conditions (of 65 per cent relative humidity at 70 deg. Fahr. temperature) permits the following conclusions: (1) No deterioration results from exposures of standard atmospheric conditions over a period of two and one-half months even when acid or alkaline perspirations are applied. (2) Sunlight exposure causes a marked deterioration in both unweighted (but dyed) and tin-weighted silks, the loss in strength in 100 hours exposure amounting to about 25 per cent for unweighted and about 50 to 75 per cent for weighted silks. (3) Acid and alkaline perspiration treatments increase the deterioration when sunlight exposures are given, so that the loss in strength in 100 hours' exposure is about 35 per cent for unweighted and about 65 to 100 per cent for weighted silk. (4) Dry cleaning solvents in no case caused any appreciable deterioration of the silk fabrics.

The introduction of the booklet deals briefly with the replacement of the sericin on raw silk and with the silk weighting process itself. What follows here is largely an abstract of the body of the report, consisting of, first, preliminary study, embracing review of the literature on deterioration, theories of deterioration, exposures, treatment with perspiration, dry cleaning and first exposure tests; second, procedure for final study, and third, test results and discussion.

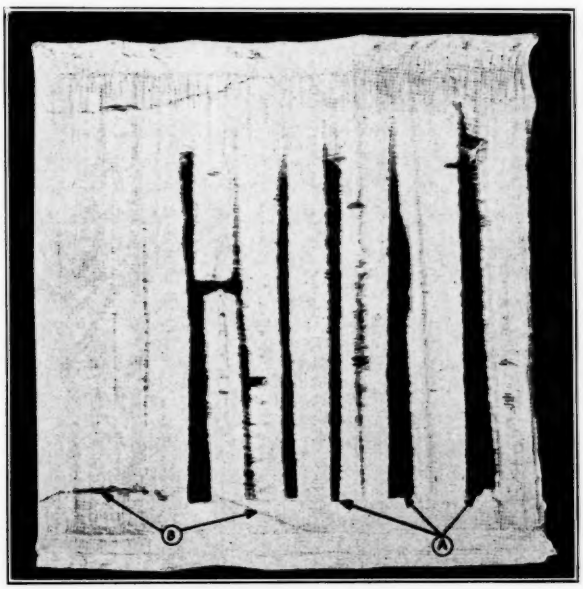
Preliminary Study

Technical literature discloses the fact that the deterioration of excessively weighted silks is well established.[1] The limitation of weighting which may be safely applied has been a much discussed question. Matthews[2] states that 18 ounces for warp yarn and 24 ounces for filling yarn is the safe limit; that is, every pound of raw silk after degumming and weighting should weight less than these limits. Chittick's[3] safety limits in general agree with Matthews's.

[1] Matthews, J. M., Textile fibers, p. 306; 1924. Farrell, W., The practice and ethics of silk weighting, The Jour. of the Textile Inst., November, 1925. Tisdale, H. R., Tin weighting skein silk and piece goods, Textile World, June 28, 1924.

[2] Matthews, loc. cit., p. 309.

[3] Chittick, James, Concerning the weighting of silk piece goods, Textile World, Aug. 22, 1925



Draperies Made from Wild Silk (Tussah), After Dry Cleaning Although Apparently in Good Condition When Received

Note absence of deterioration at top and bottom where protection from the sun was afforded by the curtain and casement of window. The strips correspond to folds in the drapes.

The researches of previous investigators, including Sisley[4], Dreaper[5], Gianoli[6], have shown that deteriorated silks show the presence of chlorides and free acid, and that silks, weighted or unweighted, readily absorb and retain acids. This acid may not only be mechanically held but may be more or less firmly combined chemically with the fiber since the latter is a basic material.

Heermann[7] states that deterioration resulted from exposure to light in the case of both weighted and unweighted silks dyed with nitro colors (as picric acid, Naphthol Yellow S, and Azoflavine FF). Nitric acid was found, and it was shown that the acid developed more quickly in the case of the weighted silk. Heermann believes that an unstable nitro compound is formed with the silk.

It is well established that paranitrotolueneorthosulphonic acid, an intermediate used in the preparation of dyestuffs, when treated in solution with sodium chloride, results in the formation of the sodium sulphonate which precipitates out, leaving a strong hydrochloric acid solution. The precipitation of the sodium salt may be attributed to the insolubility of it in strong chloride solution. Moreover, it is well known that many sulphonic acids are very strong acids.

Dyestuffs[8] are made by chemical treatment of intermediates introducing certain other groups of atoms (chromophores) with a resultant greater complexity of structure. This, in the case of many dyestuffs, is a union of two or more intermediates. Direct and acid dyestuffs, used to a large extent in dyeing silk, after dyeing may be present on the fiber in the form of the free dye acid, or as an acid salt, or as a normal salt, depending on the number of acid groups and their strength. Sulphuric acid or sodium acid sulphate, which is acid in character, may thus result from some chemical change brought about by sunlight, high humidity, etc. Also, the sodium chloride present in perspiration, sea air, etc., may combine with the sulphonic group to form the sodium salt thereof and free hydrochloric acid, or in the case of the salt of the sulphonic acid, there may occur a somewhat similar reaction.

The increased liability of metallic weighted silk to deterioration may result, especially in the presence of sodium chloride (in perspiration, sea air, etc.), from the action of the hydrochloric or sulphuric acids on the weighting itself, thus causing some reversal of the weighting process, which, if it forms stannic chloride of a sufficient concentration, will tender the silk.

The conditions most likely to effect some change in the fabric were exposure to sunlight, treatment with perspiration, ironing and dry cleaning solvents.

Procedures for testing resistance of fabric to fading resulting from perspiration had been outlined by the American Association of Textile Chemists and Colorists[9] and are in use in many laboratories, including the routine testing laboratories of the Bureau of Standards. Although essentially for testing fastness of dyestuffs, it was felt that they could be used advantageously in this study. It may be noted that although perspiration from the human body is generally acid when fresh, later, through decomposition, it becomes alkaline. The rate of decomposition depends largely on the health and race of the individual.

Dry Cleaning

With the view toward formulating laboratory procedure for dry cleaning, the plant practice was studied and the following information was ascertained.

Solvents commonly used as dry cleaning agents are gasoline, naphtha, benzol, chloroform, ether, carbon disulphide, turpentine, etc.

These solvents are chemically inert in contact with the fibers. Also, they do not alter the shaping; for example, a piece of pleated material retains the pleating in a dry solvent but loses it in water. An elaborately trimmed gown cleaned in a dry-cleaning solvent retains its form in every way, although the same article immersed in water becomes shapeless and must be shaped and ironed into form again.

At this point standard dry cleaning practice is outlined, together with data on dry-cleaning solvents and soaps. The laboratory process for dry cleaning used during this study consisted of the following steps:

Step 1.—Silk specimens were placed in glass jars containing dry-cleaning solvent to which benzine soap was added (70 grains to the gallon of stock solvent) and agitated mechanically for 45 minutes by slowly rotating the jars.

Step 2.—The specimens were removed from the soapy solvent and placed in new cleaning solvent for five minutes and rinsed free of soap.

Step 3.—The specimens were then centrifuged to remove excess cleaning solvent.

Step 4.—The specimens were then deodorized by placing in a current of air from an electric fan.

First Series of Exposure

Having available the necessary information relative to the process to be used, it was desirable to obtain some data in a preliminary way which would aid in fixing the duration of exposure and intervals at which tests should be made. For this purpose there were purchased six silk materials, five unweighted and one tin-weighted, to which were added samples from six other silk fabrics, which had been submitted by an interested manufacturer, five of which were weighted.

[4] Sisley, F., Abstracts, J. Soc. of Dyers and Colorists, p. 83; 1909.
[5] Dreaper, W. F., Abstracts, J. Soc. of Chem. Ind., p. 25; 1912.
[6] Gianoli, Chemical Zeitung, p. 105; 1910.
[7] Heermann, Chemical Zeitung, 38, p. 1381-82; 1918.
[8] Green, Arthur G., Analysis of dyestuffs, p. 4 (2nd ed.); 1916.
[9] Year Book, p. 72; 1924.

Specimens were subjected to nine treatments and exposures as listed in Table 2. All were exposed to direct sunlight for a period totaling sixty hours.[10] Breaking-strength tests were made before and after the various treatments. An additional forty hours of sunlight exposure was then made and strength results obtained.

TABLE 2

Treatments and Exposures of Weighted and Unweighted Silk Fabrics

No.	Treatment	Exposure
1	None	Sunlight
2	Heavy solvent	Do
3	Motor gasoline	Do
4	Acid perspiration	Do
5	Acid perspiration, then heavy solvent	Do
6	Acid perspiration, then motor gasoline	Do
7	Alkaline perspiration	Do
8	Alkaline perspiration, then heavy solvent	Do
9	Alkaline perspiration, then motor gasoline	Do

In this series of tests it was found that the weighted silk fabrics decreased in strength from 25 to 100 per cent; the unweighted silk decreased in some cases as much as 40 per cent, but, in general, the deterioration was of the order of 10 to 25 per cent. No loss in strength can be attributed to the dry-cleaning process.

It was noted that five hours' exposure to sunlight could be obtained on the average day, and since outer garments worn outdoors would be subjected to a similar exposure, this made a useful time subdivision for the major investigation. This period was started each day at 10.30 a. m. A total of 100 hours was thought to be a sufficient length of time for the purposes of this study.

It may be desirable to call attention to the fact that this length of exposure (100 hours) for the average garment would require in actual service a period of time aggregating six months to several years. Few garments are worn steadily day after day, and even when this is done their exposure to direct sunlight is generally of short duration.

The strip method of measuring the breaking strength was used, using an inclination balance type of machine of 150 pounds capacity, specimens 1 inch wide, distance between jaws 3 inches, and rate of speed of pulling jaw 12 inches per minute.

The weighting was determined by two different methods. Allen's[11] method was used first as follows: (1) Extract with ether in soxhlet apparatus for four hours, dry; (2) extract with alcohol for four hours, dry; (3) extract with boiling distilled water, dry and weigh; then (4) ignite the material and weigh the ash. The first three treatments extracted the non-metallic weighting, such as oil, sugar, paraffin, soap; the ash ignition was used to determine the metallic weighting.

The results of the two methods checked within 1 per cent. Tests were made separately on the warp and the filling, and the greatest difference was found to be under 2 per cent of weighting.

The analyses of the silk samples used during the second series are given in Table 4:

The treatments and exposures listed in Table 2 were then given. The sunlight exposure occurred during the period from September 9 to November 21, 1925, on the roof of the Industrial Building of the Bureau of Standards, Washington, D. C.

Duplicate samples were given similar treatments at the same time as those exposed to sunlight, but instead of exposure to sunlight they were hung in a conditioning room, which was maintained at approximately a relative humidity of 65 per cent at 70 deg. Fahr. These samples were exposed to light from an indirect lighting system about seven hours each day.

TEST RESULTS AND DISCUSSION

The deterioration of the silk was measured in terms of breaking-strength values, and for convenience in evaluation these were calculated in terms of per cent of the original strength; that is, the strength before any treatments or exposures had been given. The warp and filling results were recorded separately.

The graphs showing the results of the test indicated that no appreciable deterioration occurred as a result of exposures in conditioning room, even when treatment listed in Table 2 were given. This was to be expected, for it must be realized first that the age of the samples were unknown as far as date of manufacture was concerned, and second, that the data obtained in this phase amounted to a series of tests made over a period of two and one-half months on samples stored under almost ideal conditions. The variation from point to point in the results

TABLE 4.—*Test data on silk fabrics used in second series*

Code assigned	Type	Tin weighting	Soluble weighting	Thread count		Breaking strength (strip method)	
				Warp	Filling	Warp	Filling
		Per cent	*Per cent*			*Pounds*	*Pounds*
A	Crêpe	None.	5.0	143	80	37	12
B	do	41.8	3.2	148	82	36	14.5
C	do	55.6	2.4	146	83	39	17
D	do	59.2	3.8	147	84	41.5	20.5
E	do	62.4	2.6	208	90	48	28.5
F	Taffeta	55.6	11.4	172	88	31.5	25

All the crêpes had alternate two picks right and left twist.
The taffeta was plain woven.
Per cent of tin weighting calculated on basis of fiber alone (and not fiber plus sericin).
All were dyed except E.

[10] During summer months

[11] Allen, Commercial organic analysis, 8 (4th ed.), p. 655.

of each sample in this phase was quite marked, and the interpretations should be based on the warp, which showed much less variations than the filling. The variations of the filling from point to point on the chart may be partly accounted for by the fact that the filling strength was quite low at the start and thus variations expressed as per cent appear large.

Some consideration was also given to determining what the result of covering the silk with a cotton material during the sun exposures would be. Samples of the weighted and unweighted fabrics were treated with acid perspiration and then sewed between two layers of bleached cotton sheeting. The treatment was repeated at 20-hour intervals. These were exposed to sunlight for 100 hours and then tested. It was found that the unweighted samples decreased in strength about 35 per cent, and the weighted samples showed decreases in strength ranging from 60 to 90 per cent. The rays of the sun which caused the deterioration evidently penetrated freely through the cotton sheeting.

The tendered or deteriorated silk in each case gave an acid reaction when analyzed, and examination under the microscope showed crystallization, carbonization (partial decomposition), or acid burns. The crystalline form appears as a result of the disintegration of the fiber into minute fibrils, caused by the brittleness resulting from deterioration or the actual shearing of the fiber by the crystals from the acid or alkaline treatments.

The tendered silk, even though it had deteriorated to a point where the slightest strain broke or tore it, appeared to be in good condition, although somewhat faded; in fact, it had the same characteristic appearance as weighted silk which has been ignited. (Weighted silk when ignited leaves an ash retaining the same form as the original fabric; that is, the identity of the weave is not lost.) Even the slight whipping of the wind resulted in tearing in the latter stages of the tests, and the weight of the solvent on the fabric was at times sufficient to tear the sample when it was lifted from the liquid.

A careful study of these results shows that the dry-cleaning solvents did not affect the silk fabric; in fact, as pointed out previously, some retarding of the disintegration was evident in the early stages of the treatments. This may have resulted from a slight amount of benzine soap remaining on the fiber, which acted as a moisture repellent. From a chemical standpoint, none of the ingredients used in the dry-cleaning process contains any chlorides whatsoever, with the possible exception of a trace as an impurity in the caustic soda used in making the benzine soap, which impurity would be still further minimized because of the small amount of the soap used in the cleaning process.

Practical observations disclose the fact that vegetable and animal oil or fats and animal secretion as soil on silk weighted with tin salts, after short exposure or in the presence of heat becomes indelible.

ACID DYES SHOWN IN NEW NATIONAL FOLDER

A new forty-page color card entitled "Acid Dyes for Worsted Piece Goods," issued by the National Aniline & Chemical Company, tabulates seventy-two shades, displays them attractively on swatches and gives their fastness properties to light, washing, fulling, alkalies, etc. This is the third revised edition of the National Acid Color Card.

The text of this new card is of unusually practical value, comprising concise information on the application of the acid wool colors, notes on dyes of special properties, such as their use with various acids, and on colors used in dyeing effect threads, etc.

One distinctive feature of the text is the section devoted to a tabulation of the colors according to the effect on them of Monel metal, copper and iron It is shown by this table that almost every color listed is practically unaffected by Monel metal, while many are made duller to either a slight or considerable extent by copper and iron. Data of this nature is extremely interesting to dyers, and the National Aniline & Chemical Company is to be commended for making it a regular feature of its color cards.

DU PONT ADDS FAST SCARLET

The dyestuffs department of E. I. du Pont de Nemours & Co. are placing on the market Pontamine Fast Scarlet 4BA, a direct dyestuff which yields brilliant scarlets not only on all classes of cotton goods, but also on rayon and silk.

It shows good general fastness on all of these fibers.

When dyed on half-silk from a neutral bath it dyes cotton to a full shade and stains the silk but slightly, but when speck dyed the animal fiber is left clear.

It is suitable for printing, and can be discharged to a clear white with Sulfoxite C.

An Italian dyestuff factory, recently established at Milan under the name "Industria Chemica di Melegnano," is producing a line of vat dyes for wool, principally Diamond Black PV, and also a series of acid blacks and blacks for half silks. It is expanding its line to include series of special type dyes.

The rate for "Position Wanted" advertisements in this column is 2 cents a word—with a minimum of 50 cents per insertion. For all other types of advertisements—i. e., help wanted, machinery or supplies for sale—the rate is $5.00 per column inch or less per insertion.

SUPERINTENDENT OF DYEING

Superintendent of dyeing; graduate chemical engineer well versed in plant management methods. Experienced dyer and finisher. Specialty: vat and insoluble azo colors on cotton, rayon and silk piece goods. Now employed. Seeks more exacting responsibilities with commensurate remuneration. Reply Box 373, American Dyestuff Reporter.